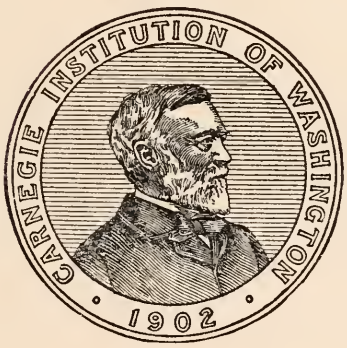
THE ABSORPTION SPECTRA OF SOLUTIONS AS STUDIED BY MEANS OF THE RADIOMICROMETER

THE CONDUCTIVITIES, DISSOCIATIONS, AND VISCOSITIES OF SOLUTIONS OF ELECTROLYTES IN AQUEOUS, NON-AQUEOUS, AND MIXED SOLVENTS

BY

HARRY C. JONES AND COLLABORATORS



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PREFACE.

The work recorded in this monograph, while apparently dealing with several subjects, is in fact closely connected, in that it all bears directly or indirectly on the present solvate theory of solution, which was proposed in the Johns Hopkins laboratory about fifteen years ago.

The work on the absorption spectra of solutions by Dr. Shaeffer and Mr. Paulus, using the radiomicrometer, led to results of the same general character as those obtained earlier by Dr. Guy and recorded in publication No. 190 of the Carnegie Institution of Washington. Solutions of some non-hydrated salts are about equally transparent with pure water, except at the bottoms of the absorption bands, where the solutions are more opaque. Solutions of hydrated salts are in general more transparent than pure water. All things considered, we regard this as the strongest evidence thus far obtained in favor of the solvate theory of solution.

The work of Dr. Smith, on the conductivity and dissociation of certain organic acids in water, is a continuation of that which has already appeared in publication No. 170 of the Carnegie Institution of Washington. The investigation by Dr. Wightman and Mr. Wiesel, on the conductivity of organic acids in alcohol, is a continuation of the work which has been in progress in this laboratory for more than ten years on the conductivity and dissociation of electrolytes in water as a solvent. (See publication No. 170 of the Carnegie Institution of Washington.) While this investigation is only preliminary, results of interest have already been obtained.

Dr. Wightman, Dr. Davis, and Mr. Holmes made a very exhaustive study of two simple salts in mixtures of alcohol and water, solutions in mixtures of these solvents showing abnormal properties.

The work by Dr. Davis and Dr. Hughes, on the properties of solutions in acetone, was taken up because of the abnormal behavior of acetone as a solvent.

The investigation by Dr. Davis and Mr. Putnam, of ternary mixtures of glycerol, acetone, and water, had in mind the fact that glycerol has a very high viscosity, water intermediate viscosity, and acetone a very low viscosity. The viscosities and conductivities of solutions in ternary mixtures of these solvents were studied. A general discussion of the results obtained, bearing on the solvate theory of solution, seemed desirable. The work as completed was published in a large

number of papers, and in a fairly large number of journals in America, Germany, England, and Switzerland. A general discussion of the results thus far obtained would render reference to the work more convenient. The last chapter of this monograph gives in concise form such a discussion and summary. A bibliography of the papers and monographs already published, bearing upon this theory, will make reference to the literature simpler.

Finally, it gives me great pleasure to thank the Carnegie Institution of Washington for the generous aid with which they have supported these investigations, and without which it would have been impossible to do much of this work.

HARRY C. JONES.

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CHAPTER I.

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF HYDRATED AND NON-HYDRATED SALTS, AS STUDIED BY MEANS OF THE RADIOMICROMETER.

By E. J. Shaeffer and M. G. Paulus.

The object in using the radiomicrometer for studying the absorption spectra of solutions was to work quantitatively. The photographic method gave us the positions of the various bands, and a qualitative, or, at best, very roughly quantitative estimate of the relative intensities of the various lines and bands. The personal equation of the photographic plate, however, always comes into play and, all things considered, we regard the photographic method as useful and reliable mainly in determining the positions of the various lines and bands.

A more important problem and one more fundamental than the determination of the positions of the lines and bands, is the measurement of the relative intensities of these lines and bands and the relative intensities of the different parts of the same band. For this purpose some instrument must be used which measures the intensity of the radiation falling upon it. We selected the radiomicrometer as best adapted to this purpose, it being a thermo-electric junction attached to a loop of non-magnetic wire, and the whole suspended in a magnetic field. The following form was constructed and used:

THE RADIOMICROMETER.

The radiomicrometer used in this investigation was built by Dr. Guy. It had a full period of 8 seconds and a sensibility of 8 cm. per square millimeter of exposed junction, candle and scale being at a distance of 1 meter. This instrument, therefore, combines very high sensibility with very short period. It had no compensating junction, and this necessitated very careful protection from changes in temperature, from air drafts, and from energy radiations in general; otherwise the zero-point would be unsteady. It was found that by incasing the instrument in a tight wooden box of such dimensions that the radiomicrometer was surrounded by a layer of cotton a foot thick, the drift of the zero-point was entirely eliminated if the temperature of the room was fairly constant. It was quite practicable to keep the room at a sufficiently constant temperature for this purpose. The accuracy of the results was greatly increased by keeping the zero-point constant. Precaution was also taken to keep the current which passed through the Nernst glower as invariable as possible. The source of electricity used was a large storage battery, which supplied a very constant current, provided

the Nernst glower was carefully protected from air-currents. This was accomplished by inclosing the glower in a tight box of heavy asbestos board. That the current must have remained invariable during the two successive readings which we had to make, to obtain the percentage transmission for any given layer of solution, is shown by the close agreement of the duplicate readings. As a rule, the duplicate results agreed with one another to within less than 1 per cent. That we could duplicate our readings so closely we regard as due to the constancy of the zero-point of the radiomicrometer and to the steadiness of the current passing through the Nernst glower. Another factor which seriously interferes with the accuracy of this work is mechanical vibrations. This effect becomes especially noticeable when the deflections of the radiomicrometer are small. By placing felt under the marble slab which served as the base of support of the instrument, and setting the radiomicrometer support on blocks of wood and cork, we were able to eliminate all mechanical disturbances except those of a very violent character. When such violent disturbances occurred, the work was temporarily discontinued and the measurements repeated.

METHOD OF PROCEDURE.

The Nernst glower carried 0.8 ampere and 120 volts. By means of an adjustable resistance we could keep the current very close to 0.8 ampere throughout this entire work. If any appreciable variation in the current was detected between the two successive readings which determined the transmission for any given layer of solution, the readings were always repeated. The light from the Nernst glower, after being rendered parallel by passing through a lens, was passed through a given layer of solution and then focused on the slit of the Hilger spectroscope.

By properly rotating the drum-head of the spectroscope, we could throw the desired wave-lengths of light on the junction of the radiomicrometer. The dispersion curve for the glass prism was carefully worked out, some of the points in the infra-red being determined by means of the water-bands. It was possible to find definite maxima of absorption for the water-bands 1μ, 1.25μ, 1.51μ, and 2.01μ. Since we worked mainly with aqueous solutions, after each series of measurements we could determine, by means of the water-bands, whether the prism had shifted or not.

Suppose it is desired to know the absolute transmission of a given solution, 20 mm. in depth, for a given wave-length of light. This was done by the following differential method, the correctness of which has already been discussed:[1] Twenty-one millimeters of the solution were placed in one cell and 1 mm. was placed in a second cell, which was exactly like the first one. The wave-length of light, whose transmis-

[1]Carnegie Inst. Wash. Pub. 190, p. 62.

sion by the solution it was desired to measure, was made to fall upon the junction after passing through the solution, by turning the calibrated drum-head to the proper point. The deflection when the deeper layer was in the path of the beam of light was noted, and as quickly as possible the cell containing the more shallow layer was placed in the position formerly occupied by the deeper layer. This was accomplished by a carefully adjusted sliding carriage. The deflection when the more shallow layer was in the path of the beam of light was noted. The deflection produced when the light passed through the deeper layer of solution, divided by the deflection when the more shallow layer was in the path of the light, gave the absolute percentage transmission of 20 mm. of the solution, for the wave-length of light in question.

In work such as this, involving as it does so many distinct and separate operations, it is highly desirable to duplicate all of the measurements. This has been done in nearly all of the work the results of which are herein recorded. In only some cases are the duplicate results given. In every series of measurements, duplications were made for certain wave-lengths of light. After filling the cells with solution or solvent, and making the necessary adjustments as accurately as possible, the percentage transmission was determined several times for wave-length λ 706. When 20 mm. of the solution or solvent was employed this was always about 95.5 per cent. After taking about ten readings farther down in the infra-red, wave-length of light λ 706 was again passed through the solution and thrown upon the junction. The transmission for this wave-length was repeatedly determined during the entire series of measurements. Usually we obtained the same percentage transmission in the two cases, to within the limit of error of the method. This showed that comparable conditions were maintained in both cells during the time required to make the intermediate readings. Duplicate results are given for the wave-lengths $\lambda = 0.706\mu$, $\lambda = 1.00\mu$, and $\lambda = 1.24\,\mu$. These were secured after the entire series of measurements had been completed. To obtain reliable readings great care had to be exercised in adjusting the cells in the carriage, so that there was the same distribution of light from the glower upon the slit when either cell was placed in the path of the light.

THE CELLS.

The cells for holding the solutions and solvent are among the most important parts of the apparatus, and the reliability of the results is largely dependent upon how they meet various requirements. Two cells were made for this work, and they were made as nearly alike as possible. Each cell consisted essentially of two brass cylinders, which telescoped neatly into one another. Glass plates were set into the ends of each cylinder by means of Wood's fusible metal, so that their surfaces were parallel to one another. The question as to whether the

plates were sufficiently plano-parallel was determined by the character of the interference fringes which they gave. These glass plates closing the ends of the cells were 1 mm. thick. We found some difficulty in procuring plates of the best optical glass which were plano-parallel. Many times when the plates were sufficiently plano-parallel for our purpose, the Wood's metal surrounding the edges of the plates would, on cooling or setting, so warp the plate that it was necessary to reset it. This often had to be repeated several times to secure the desired result.

The distance between the glass ends was regulated by means of a finely threaded nut which screwed on to the outer cylinder. Each complete revolution of this nut raised or lowered the inner cylinder just 1 mm. The nut was calibrated in 100 divisions by means of a dividing engine, and with this nut we could readily and accurately adjust the distance between the glass ends to less than 0.01 mm.

The brass cells were first heavily plated with silver, being taken out of the plating bath from time to time and thoroughly rubbed with the finest crocus powder. A heavy gold plate was then deposited on this silver surface. Unless the gold was of sufficient thickness to cover well all of the exposed portions of the Wood's metal, it was found that the concentrated and strongly hydrolyzed solutions which we studied would act upon the Wood's metal, giving rise to streamers in the solutions and often to an opalescence. This would, of course, lead to considerable error. The solutions used in making the measurements were always perfectly clear, and if any opalescence developed in them while making the measurements, the solutions were discarded and the cells were at once replated.

TABLE 1.—*Testing the two cells.*

λ	Cell I.	Cell II.	λ	Cell I.	Cell II.
706	27.5	27.5	1066	123.0	123.0
746	38.0	38.0	1138	135.5	136.0
787	50.5	50.5	1216	63.5	63.5
833	65.0	65.0	1292	65.0	65.0
886	79.5	79.0	1362	45.5	45.5
941	91.5	92.0	1429	7.0	7.0
1003	79.5	79.5			

The two cells were tested from time to time to see if, under comparable conditions, they both gave the same deflections. This was usually done by placing 10 mm. of water in each cell and noting the actual deflections as given by the radiomicrometer for the various wave-lengths of light. Table 1 contains the results for one such test. The given wave-lengths of light would be obtained by turning the drum-head of the spectrometer at intervals of ten divisions over the entire region of the spectrum which we studied. In all tests the deflections for the two cells agreed as closely as those given in table 1.

If equal depths of a concentrated aqueous solution were used in place of equal depths of pure water, a number of precautions were necessary in order that the same deflections would be obtained with the two cells. It was, of course, necessary that the solutions in both cells should remain perfectly clear. If even the slightest opalescence developed in one of the cells, the transmission in this cell would be less than in the other. It was further found that special precautions had to be taken to keep the glass ends of the cells clean. The ordinary methods of cleaning did not suffice. In filling the cells with a solution, some of the solution will usually come in contact with the outer surface of the glass plate in the larger cylinder. Even after considerable rubbing with a cleansing-cloth there will remain an almost invisible film of the crystallized salt on the plate. This was found to be sufficient to change the transmission as much as 5 per cent. Special precautions must be taken to clean the ends, otherwise comparable results could not be obtained.

EARLIER RESULTS.

It was earlier found by Jones and Guy[1] that when the product of the concentration of the solution multiplied by the depth of layer was kept constant, Beer's law did not hold for neodymium salts. Certain tentative suggestions were made in that work which, in the light of the present results, must be somewhat modified. The point in question involves the increase in the intensity of the neodymium bands with dilution. A possible explanation of this phenomenon, based upon resonance, was offered.

It was later found that there should be some correction made for the water absorption in the case of the 0.87μ band, since here the 1μ water-band began to absorb slightly. If we take into account both of these factors, together with the additional correction for the width of slit[2] that was used, it is thought that the phenomenon referred to above might be accounted for, and that Beer's law would hold for the dilute solutions of neodymium salts.

EFFECT OF SLIT-WIDTH.

The effect of the width of the slit on the character of the transmission curves for solutions of neodymium salts was not well understood. It seemed desirable that some work should be done on this problem, with the hope that we might arrive at a better understanding of this effect. It was found to be especially difficult to obtain concordant results when working with neodymium salts. This was due to the low dispersive power of the glass prism with which the Hilger spectroscope was provided, to the difficulty in accurately setting the calibrated head, and to the very narrow and sharp bands of neodymium salts. Rotating

[1]Amer. Chem. Journ., 44, 1913. [2]Carnegie Inst. Wash. Pub. No. 190, p. 70.

the calibrated drum-head one division towards the red would increase the wave-length of light about 40 Ångstrom units for the region which we studied. Even this slight increase in wave-length would often change the percentage transmission as much as 10 to 20 per cent. The tabular data bring this out very clearly. It is therefore necessary to exercise great care in setting the calibrated head which rotates the glass prism. Table 2 contains data which show the effect of increasing the slit-width, the changes that take place when the conditions for Beer's law are fulfilled, and the accuracy which is possible in setting the calibrated head of the spectroscope and in reading the deflections. We could not read the deflections closer than 0.5 mm., and in the visible red, with 0.2 mm. slit-width, the deflections were so small that the error in reading may be as much as 2 per cent. For conditions such as are indicated by this table, the minimum deflection obtained for a slit-width of 0.2 mm. was 12 mm.; that for 0.4 mm. slit-width was 63 mm.; the maximum deflection for 0.2 mm. slit-width was 69 mm.; that for 0.4 mm. slit-width was 378 mm.

We desired to use slit-widths as large as possible so as to increase the accuracy of the readings; this, however, could be done only when the wider slit-widths had but little effect on the percentage transmission.

It is desired to call attention to the duplicate results, which, in the tables, are bracketed. For each duplicate measurement the head of the spectrometer was reset and the deflection again read. The second reading was made after the series of readings had been completed, and then, after completing the second series of readings a third reading was taken for a few wave-lengths of light. The method of procedure was as follows: It was desired to measure the absolute transmission of 2 mm. of a 0.586 normal solution of neodymium chloride in water. This was done by the differential method already discussed. We place in cell I, 3 mm. of the solution and note the deflection as given by the radiomicrometer. Similarly, we place 1 mm. of the solution in cell II and note the deflection when cell II occupies exactly the same position formerly occupied by cell I. The deflection given by 3 mm. of the solution, divided by the deflection given by 1 mm. of the solution, gives the absolute percentage transmission of 2 mm. of the solution.

The solution was diluted eight times, its concentration then being 0.073 normal. To satisfy the requirements of Beer's law we would have to place in one cell 24 mm. of the more dilute solution and in the other cell 8 mm. We would then have the same number of absorbers in the path of the beam of light as we had in the case of the original, more concentrated solution. In the case of the more dilute solution we would obtain the absolute transmission for 16 mm. depth of layer. This would be comparable with the transmission obtained for 2 mm. of the more concentrated solution. Column 1 in table 2 gives the actual head-readings. In columns 2 and 3 are given the percentage

transmissions for the more concentrated and the more dilute solutions, the slit-width being 0.2 mm. Columns 4 and 5 contain the results for the two solutions, the width of the slit being 0.3 mm. Columns 6 and 7 give the results for the two solutions when the slit-width was 0.4 mm. In all of this work about 0.8 ampere of current was used.

TABLE 2.—*Results with different widths of slit.*

1 Head-readings.	Slit-width 0.2 mm.		Slit-width 0.3 mm.		Slit-width 0.4 mm.	
	2 0.586 N.	3 0.073 N.	4 0.586 N.	5 0.073 N.	6 0.586 N.	7 0.073 N.
478	100.0	96.0	100.0	96.3	100.0	96.3
478	100.0	94.0	100.0	95.5	100.0	95.6
486	78.0	69.6	80.1	72.3	80.3	75.4
487	57.0	55.8	64.3	60.3	68.0	64.5
488	47.0	46.8	51.3	48.8	56.8	57.0
489	43.5	40.4	44.1	41.0	49.4	45.7
489	44.4	39.5	44.4	41.3	49.6	46.5
489	44.4	40.4	44.7	41.5	49.3	46.4
490	49.0	48.0	50.0	45.5	50.6	47.0
490	48.0	48.0	50.0	45.5	50.8	47.4
491	63.3	60.0	58.6	54.4	58.7	55.7
492	76.6	72.5	73.4	66.7	68.8	64.5
494	94.7	88.0	92.9	81.5	86.6	81.6
500	75.6	62.2	77.7	75.0	77.7	72.4
501	58.6	54.7	65.7	59.5	68.7	62.6
502	46.3	43.5	53.3	47.7	59.4	54.5
502	47.0	43.5	53.4	48.3	60.0	54.1
503	45.4	43.0	50.0	44.5	54.3	49.7
503	44.8	43.0	49.7	44.7	54.4	49.7
503	44.2	43.0	49.4	45.0	54.4	49.3
504	58.0	53.0	55.5	50.5	55.8	52.0
504	57.3	54.2	55.4	51.0	56.0	52.3
506	79.0	74.0	77.6	70.0	71.7	67.3
517	77.3	69.4	80.8	70.7	81.1	73.0
517	76.5	69.0	81.6	71.0	81.5	72.5
518	76.6	68.0	78.6	68.6	78.9	70.3
518	75.9	68.3	78.8	68.8	78.8	70.6
518	76.4	68.7	79.3	67.5	....	69.7
519	78.3	70.3	79.7	68.4	78.0	....
519	78.3	70.7	79.9	69.0	78.3	....
519	79.2	69.7	79.6	69.3	....	70.3
520	82.4	74.0	81.7	71.1	79.3	71.0

From the transmission values given in table 3, we can gain a fairly accurate conception of the intensity of the absorption due to the water contained in 2 mm. of the more concentrated solution, and in 16 mm. of the more dilute solution. The water absorption was taken only for those wave-lengths which correspond to the centers of the neodymium absorption bands.

Tables 2 and 3 bring out several interesting points concerning the neodymium bands. The effect of increasing the slit-width is to displace the bands towards the longer wave-lengths.[1] As we approach

[1]This is due to the slit having but one movable edge, the other being stationary.

the bands the transmission is greatest with the widest slit. As we leave the bands the transmission is least with the widest slit. This is to be expected, since the spectrum lines have their centers displaced slightly towards the red with increasing slit-width. It will be readily seen that the neodymium bands are exceedingly sharp and narrow. Doubling the slit-width will, for some wave-lengths of light, change the transmission 15 per cent or more. It is clear that the centers of the bands do not become more intense with increasing slit-widths.

TABLE 3.—*Water absorption.*

Head-readings.	1.92 mm., H_2O.	15.89 mm., H_2O.	Head-readings.	1.92 mm., H_2O.	15.89 mm., H_2O.
489	99.0	96.6	504	98.0	98.0
489	99.0	95.8	518	98.0	93.1
489	99.0	96.6	518	98.0	93.3
503	99.0	98.0	518	98.0	93.3
503	99.0	98.0	520	97.0	92.5
503	99.0	98.5			

Indeed, just the opposite effect is noted. Table 2 also shows that, aside from considerations of the purity of the spectrum, the slits of the spectroscope we used should actually be of almost infinitesimal width for lines and bands as sharp and narrow as those of neodymium.

If the slit was narrower than 0.2 mm., the resulting deflections would be so small that the error in reading the scale would be considerable. The effect of the width of the slit on the absorption bands of water was also studied, and will be discussed later.

WATER ABSORPTION.

If we consider the water absorption we find that the neodymium bands increase in intensity only slightly with dilution. Take, for example, the band represented by head-reading 489; 2 mm. of solution have less than 1 per cent absorption at this point, due to the water present. It was found from the specific gravity and concentration of the solution that 95.6 per cent by volume was water. Therefore, one cell was filled with 2.87 mm. of water and the second with 0.95 mm. of water. Each cell, then, had just as much water in it as it had when filled with 3 and 1 mm., respectively, of the solution. In this way the absolute transmission for a layer of water equal to that in the 2 mm. of solution is determined.

Considering now the more dilute solution, the cell which contained 24 mm. of solution actually contained 23.83 mm. of water, the percentage of water present being 99.3. The second cell contained 7.94 mm. of water. By the differential method we thus find the transmission for a layer of water equal to that contained in 16 mm. of the more dilute solution. The particular region which we are considering is in

the neighborhood of the 0.77μ water-band. This is a very faint band, and even for the above depth of water the actual absorption is only between 3 and 4 per cent. It will thus be seen that for the first band whose center is represented by head-reading 489, the concentrated and dilute solutions absorb with equal intensity.

Wave-length of light represented by head-reading 503 is the point which indicates the center of the first neodymium band in the infra-red. With slit-width of 0.2 mm., the water contained in 2 mm. of the more concentrated solution has an absorption of 1 per cent for this particular wave-length, while the water contained in 16 mm. of the more dilute solution has an absorption of 2 per cent. Here, as in the case of the other bands, the intensity of the bands for the dilute and concentrated solutions is the same.

TABLE 4.—*Testing Beer's Law.*

λ	Conc. 0.6 normal, depth 2 mm.	Conc. 0.75 normal, depth 16 mm.	λ	Conc. 0.6 normal, depth 2 mm.	Conc. 0.75 normal, depth 16 mm.
702	100	100	803	39.3	39.8
702	100	100	803	39.3	39.3
732	63.5	61.3	807	59.5	56.5
736	55.0	52.5	807	60.5	56.3
739	41.6	39.0	813	76.3	72.0
739	41.6	38.0	817	84.0	80.0
743	40.5	37.0	869	84.0	77.0
743	40.5	36.8	869	83.5	76.3
749	.....	44.5	875	73.5	65.5
753	66.5	64.2	875	73.8	66.0
756	82.0	74.5	880	76.5	68.5
764	94.3	90.0	880	77.0	69.0
789	73.5	66.7	885	86.0	77.3
794	42.3	42.3	890	93.0	81.7
799	34.7	31.2			
799	34.7	32.5			

Head-reading 518 marks the position for the last neodymium band we could study. The wave-length of light corresponding to this band would be approximately 0.87μ, which is sufficiently close to the 1μ water-band for the dilute solution to cause considerable absorption on account of the water present. For this wave-length 16 mm. of the more dilute solution has about 7 per cent absorption due to water; whereas the 2 mm. of the more concentrated solution has 2 per cent absorption at this wave-length. It will thus be seen that only in the case of this one band is there an increase in intensity with dilution. The more dilute solution has a band which is nearly 3 per cent more intense than that for the more concentrated solution.

It should also be noted that the absorption bands of the more dilute solution are broader than those of the more concentrated. This is shown by the fact that the percentage transmission of the more dilute solutions are always lower than those of the more concentrated. There is no evidence of a shift in the bands for the dilute solution.

Owing to the large number of possible sources of error, it was regarded as desirable to repeat the work bearing on the point under discussion. This was done three times; and that the results obtained are very concordant can be seen by comparing table 4 with table 3. The slit-width used was 0.2 mm. The depths of layers were the same as in table 3, and the concentration of the new solution was six-tenths normal.

The results seem to justify the conclusion that the intensities of the bands for both the dilute and concentrated solutions are practically the same, and that Beer's law holds fairly well for solutions of neodymium chloride. The bands in the case of the more dilute solution are broader and only very slightly more intense than for the more concentrated.

EFFECT OF SLIT-WIDTH ON THE ABSORPTION OF LIGHT BY WATER.

It will be remembered that increasing the width of the slit greatly changed the transmission of salts of neodymium. Since we were making an extensive study of the water-bands, it was desired to know what changes would take place in the transmission of water with increasing slit-widths. The 1μ water-band compared with the neodymium bands is relatively broad, and the 1.25μ water-band is very broad, it being difficult to find accurately a maximum of absorption. To study the 1μ water-band a depth of 20 mm. was employed, while 10 mm. sufficed to study the 1.25μ band of water.

TABLE 5.—*Effect of slit-width.*

1μ water-band.				1.25μ water-band.			
λ	Slit-width 0.2 mm.	Slit-width 0.3 mm.	Slit-width 0.4 mm.	λ	Slit-width 0.2 mm.	Slit-width 0.3 mm.	Slit-width 0.4 mm.
941	71.5	72.6	74.8	1066	73.5	73.5	72.9
952	63.5	62.8	62.4	1138	67.5	70.0	69.0
965	51.6	52.7	57.6	1216	24.7	26.0	28.3
978	41.6	42.5	47.0	1231	23.5	23.2	24.9
984	38.1	38.8	44.0	1238	23.2	23.0	24.0
990	35.6	36.6	40.3	1246	23.1	22.9	23.8
996	34.6	35.1	38.8	1254	23.1	22.9	23.2
1003	34.8	35.4	37.4	1261	23.2	22.8	23.1
1010	35.5	36.1	37.6	1277	23.4	23.6	23.8
1017	37.4	37.4	38.4	1292	24.4	24.3	24.4
1066	59.5	59.3	61.8	1362	14.4	16.4	16.6
1138	55.0	54.8	57.0				

When the bands are as wide as the 1μ and 1.25μ water-bands, it will be seen from table 5 that slit-widths as great as 0.3 mm. can be employed without causing any appreciable difference in the intensity of the absorption. The slit should, however, be kept as narrow as possible, and as we could easily make fairly accurate measurements in this region with narrow slits, we determined to use in all of the work described below a slit-width of 0.2 mm.

THE ABSORPTION OF LIGHT BY WATER AS AFFECTED BY HYDRATED AND BY NON-HYDRATED SALTS.

It was found by Guy, Shaeffer, and Jones[1] that the absorption of light by water was changed by the presence of hydrated salts which themselves had no absorption. Solutions of non-hydrated salts of equal concentration did not appreciably affect the power of water to absorb light. The results obtained by the above-named authors were considered by them as strong evidence in favor of the solvate theory of solution as proposed in this laboratory about 15 years ago.

That water of hydration should absorb so differently from an equal amount of uncombined water was regarded as a fact of some importance, especially in its bearing on the solvate theory of solution, and one deserving very careful study. Since the work recorded in the first paper was essentially preliminary in character, it was decided to repeat and extend this work with our improved apparatus, taking advantage of what we had recently learned from experience in connection with such work. This seemed all the more desirable in that our earlier results had been interpreted in a different manner by Livens.[2] The most recent work gives results confirming the belief that our original interpretation was correct.

The earlier work showed clearly that concentrated solutions of such hydrated salts as calcium chloride, magnesium chloride, and aluminium sulphate, which themselves had no absorption over the region of the 1μ and the 1.25μ water-bands, had a very different transmission curve from that of a layer of water equal in depth to the water in the solution in question. For some wave-lengths of light the transparency of the solution was considerably greater than that of an equal amount of pure water. It was concluded that *combined water has less power to absorb light than free water.* No such marked effect could be noted when studying the absorption of aqueous solutions of such non-hydrated salts as ammonium chloride, ammonium nitrate, and potassium chloride, even when the solution was of five normal concentration. For non-hydrated salts the curves for the solution and for water were nearly identical. It was therefore clear that combined water had very different action on light from ordinary free water.

We have repeated practically all of the earlier work dealing with this phase of our problem, and have also duplicated a very large part of our own bearing upon it. It is a matter of some difficulty to avoid considerable errors in work of this character, and for this reason it was considered desirable to make duplicate measurements as often as possible. That some idea may be gained as to the accuracy with which we could repeat our work, we give in a number of cases the results of such duplicate measurements.

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[1]Carnegie Inst. Wash. Pub. No. 190. Phys. Zeit., **14**, 278 (1913). [2]*Ibid.*, **14**, 660 (1913).

METHOD OF PROCEDURE.

Suppose we wished to study a five normal solution of calcium chloride. From the known concentration of the solution and its specific gravity, we can readily calculate the volume percentage of water which the solution contains. At 20°, the temperature at which all of this work was done, it was found that the above-named solution contains about 90 per cent of water. The 1μ water-band is of such intensity that 20 mm. of water are ample for its study. The maximum absorption at the center of the band, for such a depth of layer, is about 60 per cent. We can study any changes better when the absorption is not so intense as to give small deflections. Furthermore, the deflections given by the radiomicrometer under these conditions would be sufficient to allow accurate readings. In all of this work, unless otherwise stated, the width of the slit was 0.2 mm., and the current 0.8 ampere. Under these conditions the deflection for 20 mm. of water or solution would, at the point of maximum absorption or the center of the band, be over 60 mm.

The absolute transmission for 20 mm. of the solution of calcium chloride would be determined according to the principle already outlined. Its transmission curve could then be compared directly with that for 18 mm. of pure water. A layer of water of this depth absorbs so intensely at 1.25μ, that it would be impossible to study under these conditions the intense 1.25μ water-band. If 10 mm. of solution are used, the 1.25μ water-band can be studied very satisfactorily, the absorption at the center of the band being about 65 per cent and the minimum deflection at this point being close to 70 mm. There are, then, four transmission curves for each salt—one for the solution and one for the solvent as the result of studying the 1μ water-band, and one for the solution and one for the solvent when studying the 1.25μ water-band.

THE RESULTS.

Table 6 contains the results of two series of measurements with magnesium chloride. The second series was made about four weeks after the first. The transmissions are those of 20 mm. of the solution.

In table 7 are given the results for two series of measurements with potassium chloride. New solutions were made up for the second series of measurements. These results show that the work can be repeated with a fair degree of concordance.

Tables 6 and 7 also show that there is a marked difference between the transmission of the hydrated salt (magnesium chloride) and a layer of water equal in depth to that in the solution. No such difference exists in the case of potassium chloride, a typical non-hydrated salt.

These differences come out most clearly for those wave-lengths of light which are most strongly absorbed. Consider the region about the 1μ band, table 6, say at 1.2μ, where the deflections are fairly large

and the scale can be accurately read; we see that for potassium chloride the difference between the percentage transmission for the solution and for the solvent is only 1 part in 23, whereas for magnesium chloride, figure 1, it is nearly 7 parts in 26, or a difference of about 25 per cent. Table 6 brings out another point of considerable interest. If we consider the center of the 1μ band, which is the region of maximum absorption, it will be seen that for potassium chloride the solution

TABLE 6.—*Depth of cell 20 mm. Magnesium and potassium chlorides.*

λ	KCl 3.5 N.	H_2O.	$MgCl_2$ 4.49 N.	H_2O.	$MgCl_2$ 4.49 N.	H_2O.
706	98.4	98.0	96.4	97.3	96.4	96.4
706	98.4	98.0	95.3	97.3	97.3	97.3
746	93.6	96.0	90.3	94.9	93.7	93.7
766	92.5	94.5	93.7	95.4	92.3	94.6
770	....	....	92.8	94.8	91.6	95.1
774	....	....	92.0	95.7	92.8	93.9
778	....	....	90.3	94.3	91.2	93.1
787	93.5	94.3	92.0	96.2	94.4	95.3
809	96.5	96.5	92.2	95.8	92.7	95.1
833	93.3	94.0	93.0	94.0	93.6	93.5
857	90.7	92.1	88.9	91.8	91.2	91.6
886	90.0	90.0	88.5	90.4	90.4	89.9
913	89.8	88.5	85.3	88.7	87.3	88.3
941	81.5	81.3	80.6	79.7	82.3	79.7
952	72.7	72.3	74.6	70.0	76.7	71.4
965	63.7	61.2	65.6	59.0	67.4	60.8
972	56.8	56.3	60.7	54.4	61.7	54.7
978	51.8	51.3	56.2	49.7	56.6	50.8
984	48.5	47.8	52.7	46.6	53.3	47.3
990	45.2	45.2	49.4	45.1	49.6	45.3
996	44.3	45.0	46.8	44.7	47.0	44.6
1003	43.8	44.6	46.0	44.9	46.0	45.5
1003	43.8	45.0	47.2	45.3	46.3	45.3
1010	45.8	45.8	45.6	46.8	46.0	46.5
1017	46.7	47.5	46.7	48.3	46.8	48.4
1024	50.0	50.0	48.7	51.3	48.6	50.3
1029	52.6	52.5	50.7	53.7	59.9	52.9
1035	55.9	55.2	53.3	57.0	52.8	55.3
1041	59.2	58.7	56.2	60.0	55.5	58.4
1053	66.2	64.8	62.2	66.3	61.6	64.3
1066	71.8	70.3	66.7	71.5	65.3	68.7
1081	75.3	73.2	70.9	74.3	68.7	73.3
1095	75.6	74.8	71.5	75.7	71.2	74.3
1110	75.3	74.3	70.4	74.2	74.4	73.4
1123	73.0	71.5	67.3	70.2	64.4	71.2
1138	66.7	65.8	63.3	64.1	63.4	64.8
1146	62.4	61.0	....	....	....	....
1153	57.3	56.0	56.6	53.7	57.3	55.2
1161	52.1	49.6	51.6	47.4	52.8	50.0
1168	45.8	44.7	46.8	41.7	48.6	43.0
1175	39.5	38.3	41.5	34.8	43.7	37.0
1183	33.8	32.5	36.2	29.5	37.3	31.8
1192	28.5	27.2	30.4	24.5	32.2	26.4
1200	22.8	21.9	26.1	19.6	27.4	21.6
1208	18.2	17.1	21.3	16.1	23.2	17.4
1216	14.5	14.7	17.8	14.2	19.1	14.5
1224	12.7	12.7	14.8	12.6	15.7	12.6
1231	12.1	12.1	13.4	11.8	13.5	11.8

absorbs more intensely than the solvent. Just the opposite effect is noted for magnesium chloride, in which case the solution absorbs less intensely. The same relation manifests itself again in the case of the 1.25μ band, as can be seen in figure 2 and in table 7.

The curves are plotted in all cases from the data given in the tables. The heavier line indicates the transmission curve for the solution; the lighter represents that for the solvent.

Tables 6 and 7 are plotted as curves for magnesium chloride in figures 1 and 2.

TABLE 7.—*Depth of cell 10 mm. Potassium and magnesium chlorides.*

λ	KCl 3.5 N.	H_2O.	KCl 3.5 N.	H_2O	$MgCl_2$ 4.49 N.	H_2O
706	97.0	99.0	98.3	98.3	98.3	96.5
706	97.0	99.0	98.3	98.3	98.1	96.5
1153	72.9	73.6	73.3	73.5	74.8	72.7
1168	63.2	63.4	63.1	63.4	67.2	62.3
1175	58.2	58.3	58.2	58.3	62.6	57.4
1183	52.5	53.6	52.0	53.5	58.5	52.9
1192	47.8	48.5	47.0	48.5	55.1	48.7
1200	42.7	44.4	42.4	44.5	49.7	44.3
1208	38.3	40.2	37.7	40.0	45.8	40.0
1216	34.8	37.2	34.0	37.4	41.7	37.0
1231	33.0	34.5	31.6	34.6	36.9	34.0
1238	31.6	33.2	31.0	34.2	35.5	33.8
1246	31.0	33.2	31.4	34.1	34.2	33.3
1246	31.2	33.5	31.6	34.0	34.2	33.3
1254	....	....	....	....	33.6	33.8
1261	32.7	33.3	33.3	34.2	33.4	34.3
1269	33.4	34.4	33.4	35.4	33.8	34.6
1278	34.6	34.6	34.8	34.3	34.9	35.4
1292	36.1	35.1	36.6	35.4	35.0	35.7
1306	37.0	35.1	37.6	35.2	35.1	35.4
1313	37.2	34.7	38.0	35.1	35.6	35.2
1321	36.9	33.4	37.3	33.8	34.3	34.3
1334	35.7	32.3	35.0	32.3	33.0	32.2
1348	32.8	29.1	31.7	28.9	31.0	28.8
1362	28.7	24.4	27.5	24.2	28.2	24.5
1377	24.2	19.7	24.5	20.2	23.6	20.4
1388	19.0	15.8	18.0	15.8	19.5	15.4
1400	15.1	12.5	14.0	12.2	15.5	11.9
1414	11.3	10.0	10.0	9.5	14.1	11.7

Tables 8 and 9 contain the percentage transmissions for the three hydrated salts, magnesium bromide, magnesium sulphate, and zinc sulphate. Where the light is intensely absorbed as at 1.2μ, and the depth of layer is 20 mm., the solutions are over 30 per cent more transparent than the solvent. In the case of magnesium chloride, bromide, sulphate, and zinc sulphate at the centers of both the 1μ and the 1.25μ bands (figs. 1 to 8) the solutions are the more transparent. This difference is very pronounced in the case of the two sulphates, especially with magnesium sulphate. Here the difference for the 1μ band is about 18 per cent, and for the 1.25μ band about 20 per cent.

The data for the two hydrated salts (zinc nitrate and calcium chloride) are recorded in tables 10 and 11. The last three columns of table 10 contain triplicate results for 20 mm. of water, while the last three columns in table 11 contain triplicate results for 10 mm. of water. To save time, we proposed to determine carefully the transmission curve for 20 mm. of water, and then use the results in our

TABLE 8.—*Depth of cell 20 mm. Transmission of hydrated salts.*

λ	$MgBr_2$ 3.60 N.	H_2O.	$MgSO_4$ 2.14 N.	H_2O.	$ZnSO_4$ 2.92 N.	H_2O.
706	98.0	95.7	96.5	96.5	96.4	96.6
706	98.0	95.7	96.5	96.7	96.4	96.6
725	....	....	94.4	95.8	95.3	94.3
746	91.3	94.8	93.5	92.7	94.7	94.0
766	95.5	94.6	93.5	92.7	94.2	93.6
774	....	....	....	....	....	94.0
778	90.5	92.8	....	....	92.5	94.2
787	....	....	92.5	93.6	93.8	95.4
809	90.5	93.6	93.5	96.0	94.5	95.2
833	91.5	94.4	93.0	92.3	92.3	92.3
857	89.0	91.0	90.5	89.8	91.4	91.0
886	86.6	89.7	89.0	87.5	89.2	90.2
913	85.7	87.3	86.2	85.3	86.8	87.4
941	78.8	79.7	78.6	76.0	79.6	....
952	72.8	71.3	72.3	66.8	74.2	69.5
965	62.7	58.6	63.4	54.8	64.8	58.1
972	....	....	58.4	48.8	59.2	52.7
978	52.0	48.2	53.3	44.3	55.2	47.7
984	47.6	45.3	50.0	40.3	51.0	44.0
990	45.7	43.5	47.2	38.6	48.6	42.4
996	44.7	42.8	45.3	37.1	46.4	41.4
996	....	....	45.3	36.9	45.8	41.3
1003	45.2	43.3	44.6	36.9	45.6	41.6
1003	44.3	43.3	....	....	....	....
1010	45.6	44.8	45.2	38.3	45.9	43.0
1017	46.0	46.4	46.2	40.0	46.6	45.0
1024	48.3	48.8	48.4	42.7	48.7	47.3
1029	51.7	51.6	49.4	45.2	50.7	50.4
1035	55.0	54.6	....	....	52.0	52.9
1041	57.0	58.0	55.5	51.8	54.7	56.5
1053	66.6	64.6	59.8	58.7	59.2	64.3
1066	70.0	69.3	65.2	63.6	62.8	68.1
1081	72.3	73.0	67.8	68.0	66.3	71.4
1095	75.8	74.6	70.0	70.3	68.4	72.3
1110	73.5	73.6	69.3	68.4	67.6	71.0
1123	73.0	69.2	66.5	65.5	....	....
1138	67.6	63.9	62.0	59.8	62.5	61.2
1146	....	....	....	....	59.6	56.4
1153	61.0	53.5	54.5	49.4	55.8	51.2
1161	....	....	....	....	51.7	45.4
1168	53.3	39.4	44.3	38.8	46.4	39.1
1175	45.4	32.6	38.7	32.3	40.8	32.7
1183	....	....	33.2	26.2	35.6	27.1
1192	31.6	21.1	28.3	21.3	30.3	21.8
1200	25.2	17.0	23.1	16.3	25.3	19.3
1208	19.6	14.1	19.4	12.9	21.3	13.9
1216	16.4	12.0	15.4	10.1	17.7	11.4
1224	15.2	11.4	13.3	8.4	15.1	10.2
1231	12.8	10.6	11.5	7.3	13.0	9.3

subsequent work. The cells containing the solution could then be so adjusted that they would contain just as much water as was present when the percentage transmissions for 20 mm. of water, that is 21 mm. in one cell and 1 mm. in the other, were determined.

It was found that, although this procedure would save much time and labor, it can not be recommended where it is desired to do accurate work, since the conditions would not be as nearly comparable as they would be if the absorption of the solvent was determined immediately

TABLE 9.—*Depth of cell 10 mm. Transmission of hydrated salts.*

λ	$MgBr_2$ 3.60 N.	H_2O.	$MgSO_4$ 2.14 N.	H_2O.	$ZnSO_4$ 2.92 N.	H_2O.
706	97.0	98.4	96.5	96.6	99.0	97.0
706	97.3	98.4	96.5	96.6	99.0	97.0
1138	79.1	77.3	78.6	76.1	....	....
1153	73.6	69.7	72.6	69.0	84.9	75.6
1168	66.2	59.8	64.8	58.0	74.6	65.6
1175	61.2	54.1	59.0	52.3	70.3	60.0
1183	55.8	48.3	55.5	47.1	65.3	55.3
1192	51.5	44.1	49.6	42.2	59.7	51.3
1200	46.4	39.3	45.4	36.8	56.4	46.6
1208	41.6	36.6	41.4	32.8	50.5	43.6
1216	38.9	33.7	38.2	29.8	47.5	40.4
1224	36.2	33.0	35.6	27.8	....	....
1231	34.4	31.8	34.6	27.1	42.6	39.1
1238	33.3	31.3	32.9	26.0	41.7	38.1
1246	33.3	31.2	32.1	25.9	41.4	38.2
1246	32.8	31.1	32.4	25.7	41.7	38.1
1254	31.3	31.6	31.7	25.9	41.7	38.5
1261	34.3	31.7	31.5	26.0	42.2	39.3
1269	34.4	32.0	31.3	26.4	42.7	39.7
1278	34.8	32.2	30.9	26.6	43.3	40.3
1292	36.2	32.3	30.8	27.5	43.7	40.7
1306	37.6	32.8	30.3	27.9	43.7	39.7
1313	37.0	32.4	30.1	26.9	43.1	39.1
1321	37.7	31.3	29.2	26.7	42.7	36.4
1334	35.8	28.8	27.5	25.1	37.8	32.6
1348	32.5	25.1	25.2	22.8	33.4	27.4
1362	27.5	20.6	19.9	19.2	28.7	23.3
1377	22.8	16.4	17.4	15.7	22.9	17.5
1388	17.7	12.2	13.8	11.7	17.4	13.1
1400	13.4	9.0	10.1	9.4	13.6	9.7
1414	9.0	6.0	7.9	6.0	9.6	6.9
1429	6.3	5.3	5.2	3.3	....	....

after that of the solution. The latter procedure was therefore adopted. It will be noted that the percentage transmissions for the three series of measurements with pure water (tables 10 and 11) are very concordant for both the 1μ and the 1.25μ bands.

Zinc nitrate, unlike the hydrated chlorides, bromides, and sulphates, presents an apparent exception in the case of the 1μ band (fig. 9). At the center of this band the solution has the greater absorption, although the difference between the absorption of the solution and that of the solvent is not large. The same phenomenon makes its appearance in

the case of magnesium nitrate, the work having been three times repeated and the same results obtained in every case. We desire to arrest attention to this apparent peculiarity of the hydrated nitrates. The 1.25μ band (fig. 10) does not show this peculiarity. The results here are of the same general character as in the cases of the other hydrated salts with which we worked. There are differences as great as 25 per cent between the absorption of the solution and that of the sol-

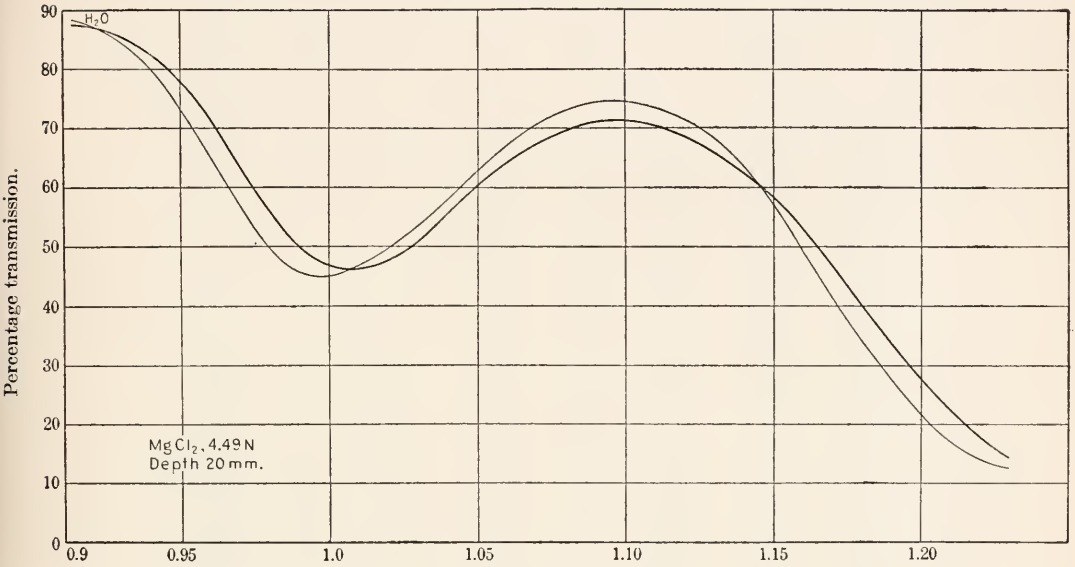

FIG. 1.—Wave-lengths.

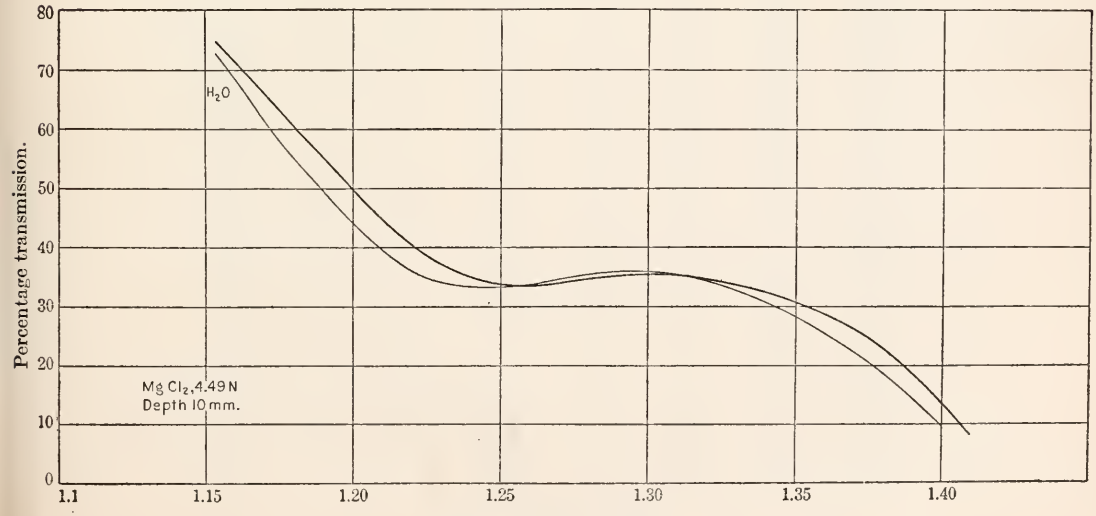

FIG. 2.—Wave-lengths.

vent in the neighborhood of 1.2μ (fig. 9) where the absorption is intense, as it is approaching the center of the 1.25μ water-band. Here the solution is the more transparent, as is generally the case with hydrated salts.

The curves for calcium chloride (figs. 11 and 12) deserve careful study. The solution is more transparent than the solvent for every wave-length of light that we studied. This holds true for both of the

TABLE 10.—*Depth of cell 20 mm. Transmissions of zinc nitrate, calcium chloride, and water.*

λ	$Zn(NO_3)_2$ 4.30 N.	H_2O.	$CaCl_2$ 4.78 N.	H_2O.	H_2O.	H_2O.	H_2O.
706	99.0	94.1	97.1	96.3	96.5	96.5	96.3
706	99.0	95.6	97.1	96.4	96.5	96.5	96.0
746	99.0	90.3	96.9	96.2	....	....	....
766	95.6	90.9	95.6	95.5	....	....	....
770	95.8	92.9	94.1	96.7	....	....	....
774	96.0	93.0	94.1	94.6	....	....	....
778	97.2	94.8	95.2	95.7	....	....	....
787	96.2	94.4	93.8	96.1	....	....	....
809	96.7	94.4	95.3	95.7	....	....	....
833	96.2	93.6	95.3	94.6	....	....	....
857	94.6	93.7	91.9	91.9	....	....	....
886	92.6	88.8	91.3	90.9	91.1	91.4	90.7
913	88.7	88.0	89.7	88.1	87.9	88.1	87.9
941	82.7	79.2	82.7	79.3	78.5	78.7	79.5
952	77.5	72.4	75.7	70.9	69.9	70.3	70.8
965	67.8	61.0	66.7	59.5	58.2	58.4	59.5
972	62.6	57.3	60.7	54.5	53.0	54.0	54.8
978	57.3	54.3	54.9	50.3	49.6	49.3	49.7
984	52.3	50.7	50.7	46.6	46.8	47.0	46.4
990	48.7	48.2	47.3	44.4	44.7	46.3	44.7
996	47.2	47.3	44.8	43.5	44.4	43.9	43.5
1003	45.6	47.6	44.3	43.7	45.2	45.1	44.5
1003	45.7	47.3	44.3	42.4	44.8	44.9	44.4
1010	46.2	48.7	44.7	44.4	46.2	46.1	46.3
1017	48.3	50.6	46.8	45.8	47.8	47.8	47.7
1024	50.4	51.4	48.7	48.3	50.2	49.7	49.4
1029	53.2	55.5	52.0	51.2	53.7	52.7	52.6
1035	55.8	57.7	55.4	54.1	56.2	56.3	55.2
1041	58.8	60.7	61.7	57.4	59.3	58.9	60.3
1053	68.8	66.8	66.5	63.2	65.3	66.2	65.2
1066	68.8	70.6	71.8	68.9	70.7	70.6	69.9
1081	72.2	73.7	74.7	71.6	74.6	73.3	73.5
1095	73.3	75.1	76.2	71.3	76.2	75.0	75.0
1110	74.0	73.7	74.5	71.2	74.5	73.3	72.7
1123	74.3	70.8	72.4	67.2	71.3	70.3	70.7
1138	69.3	65.7	67.7	61.0	64.1	63.5	64.0
1146	....	....	64.7	55.5	59.5	58.3	58.9
1153	64.3	56.3	59.8	49.7	53.6	52.8	53.3
1161	59.0	50.3	54.9	43.3	47.7	47.2	47.1
1168	53.8	44.7	48.7	37.3	41.7	40.7	43.6
1175	47.7	38.0	42.5	30.4	35.2	35.2	34.3
1183	42.0	32.9	37.4	24.4	30.5	29.2	29.7
1192	36.7	28.1	30.9	19.9	25.2	24.3	24.2
1200	30.4	23.2	25.7	15.0	20.0	19.8	19.5
1208	25.2	19.2	21.3	13.1	16.7	15.7	16.0
1216	21.1	16.4	17.0	11.3	13.9	13.3	13.5
1224	18.4	15.1	14.3	10.9	....	....	....
1231	16.2	14.7	12.9	10.2	....	....	....

water-bands, and there is no evidence which indicates that a shift has taken place, as is apparently the case with a few of the other bands for hydrated salts. Whenever there is a shift of the band for a hydrated salt, it is always towards the red. Near the end of the 1μ water-band for calcium chloride (fig. 11), the solution is about 40 per cent more transparent than the solvent. This is the greatest difference found with any of the salts that we studied. Near 1.3μ (fig. 12), which is close to the 1.25μ water-band, the solution is over 35 per cent more trans-

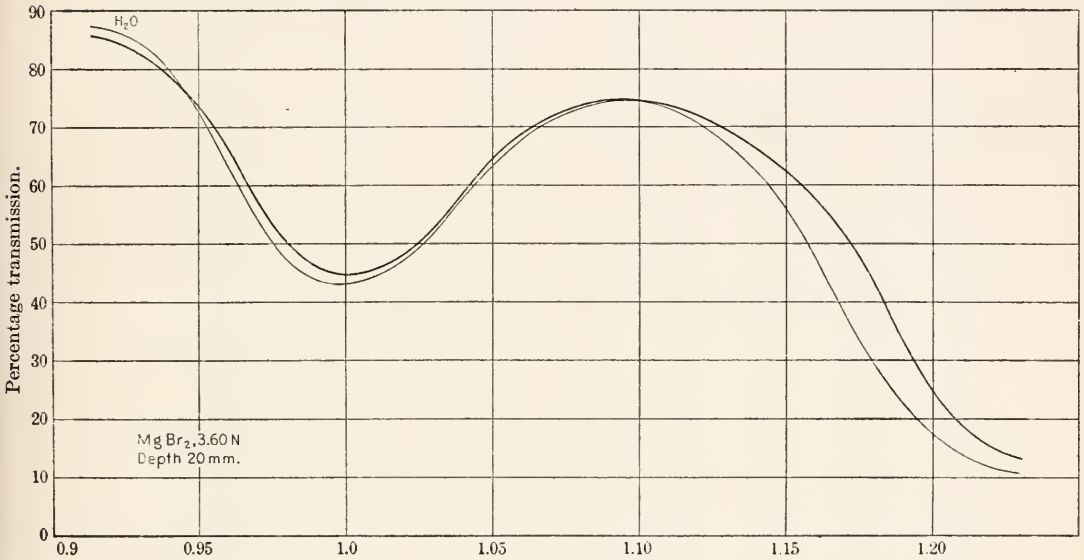

FIG. 3.—Wave-lengths.

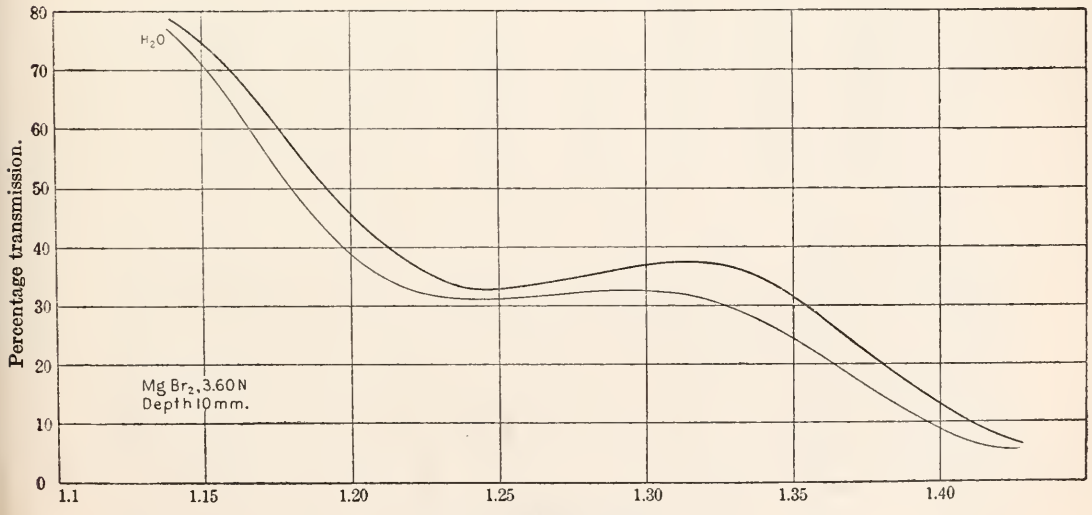

FIG. 4.—Wave-lengths.

parent than the solvent. No such differences were found at or near the 1.25μ water-band for any of the other hydrated salts that were studied. The solution of the calcium chloride used was nearly 5 times normal, and it was found that the above-named differences increase with increase in concentration. This was expected, since the total amount of combined water increases with the concentration of the solution.

The first column of table 12 contains the percentage transmissions for 20 mm. of water, while that of table 13 gives the transmissions for 10 mm. of water. The figures given are the averages of several series

TABLE 11.—*Depth of cell 10 mm. Transmission of zinc nitrate, calcium chloride, and water.*

λ	$Zn(NO_3)_2$ 4.30 N.	H_2O.	$CaCl_2$ 4.78 N.	H_2O.	H_2O.	H_2O.	H_2O.
706	99.0	97.0	98.6	98.0	98.3	98.5	98.3
706	99.0	97.0	98.6	98.0	98.3	98.5	98.3
1153	84.9	75.6	75.6	71.2	71.3	70.5	70.7
1168	76.4	65.6	66.8	61.3	61.0	59.8	59.7
1175	70.3	60.3	61.3	55.8	55.3	54.2	54.0
1183	65.3	55.3	56.2	50.3	50.0	48.6	49.0
1192	59.7	51.3	52.6	45.5	45.3	44.2	44.5
1200	56.4	46.6	46.7	41.3	40.7	39.8	40.0
1208	50.5	43.6	42.7	37.6	37.2	36.9	37.2
1216	47.5	40.4	39.4	34.9	35.4	35.1	34.9
1231	42.6	39.1	34.3	33.6	33.8	33.4	33.1
1238	41.7	38.1	34.1	32.8	33.2	33.0	33.2
1246	41.4	38.2	33.9	32.4	33.7	33.4	33.5
1246	41.7	38.2	33.9	32.4	32.6	33.7	33.4
1254	41.7	38.5	34.3	32.4	34.0	34.2	33.6
1261	42.2	38.8	34.9	32.9	34.3	34.1	33.8
1269	42.7	39.3	36.1	33.3	....	....	....
1278	43.3	39.7	37.1	34.0	35.7	34.9	33.7
1292	43.3	40.3	39.4	34.7	35.8	35.7	35.3
1306	43.7	40.7	40.5	34.5	35.5	35.1	35.1
1313	43.7	39.7	....	....	....	....	....
1321	43.1	39.1	41.3	32.4	33.5	32.8	34.2
1334	42.7	36.4	39.1	29.8	30.4	30.4	31.0
1348	37.8	32.6	36.1	26.0	25.7	25.8	25.7
1362	33.4	27.4	31.6	20.6	21.0	21.1	21.8
1377	28.7	23.3	26.2	16.3	16.2	16.3	17.2
1388	22.9	17.5	20.9	12.2	11.6	12.8	12.3
1400	17.4	13.1	15.1	8.9	....	....	....
1414	13.6	9.7	12.1	6.3	....	....	....

of measurements. Three of these series are given in tables 10 and 11 These transmissions of the solvent are to be compared with the two series of results for magnesium nitrate and sodium nitrate, and with that for ammonium bromide. A sufficient depth of solution was used to contain 21 mm. of water in one cell and 1 mm. of water in the second cell, these being the depths of layers employed in determining the percentage transmissions for 20 mm. of the solvent. In obtaining the results recorded in table 13, one cell had enough solution to contain 11 mm. of water, while the second had enough solution to contain

1 mm. of water. This procedure saved in this case the necessity of making a series of measurements with the solvent.

Magnesium nitrate presented so many peculiarities that the work with this salt was repeated three times, starting in every case with a new solution. The same general results were always obtained. The curve for the 1μ band (fig. 13) was plotted from data not recorded in this paper. The concentration of the solution was 3.80 normal, and, as in other cases, 21 mm. of solution were placed in one cell and 1 mm.

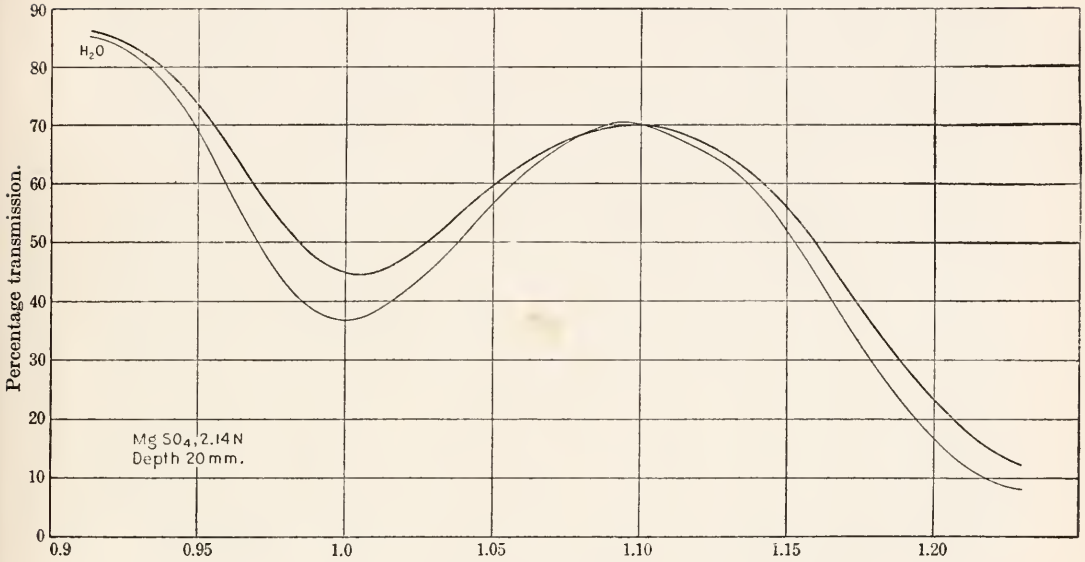

FIG. 5.—Wave-lengths.

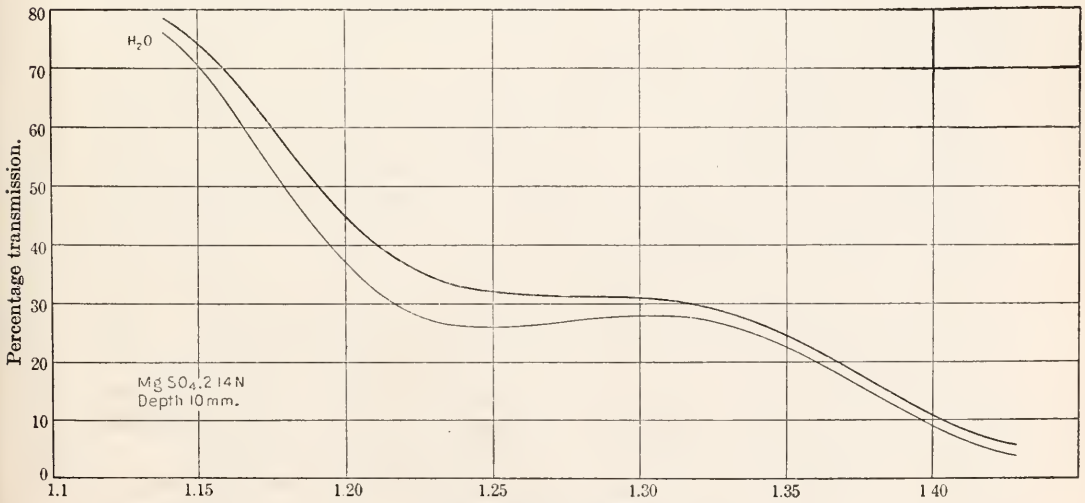

FIG. 6.—Wave-lengths.

in the other. The solution curve for the 1.25μ band (fig. 14) was plotted from the data given in the second column of table 13.

Magnesium nitrate (like zinc nitrate, the other hydrated nitrate which we studied) shows the peculiarity that at the center of the 1μ band (fig. 13) the solution is less transparent than the solvent. The difference in this case is quite pronounced. At the center of the 1.25μ band (fig. 14) the solution and solvent have about the same transmission, whereas the absorption of zinc nitrate (fig. 10) at this point conforms to the general characteristics of the bands for the other hydrated salts. Magnesium nitrate presents another curious feature, which is not present in the results for any of the other hydrated salts. The difference between the percentage transmissions for the solution and for the solvent is at no point very great. The data given in table 12 for the 1μ band show that for wave-lengths of light near 1.2μ the solution is actually several per cent less transparent than the solvent. This is the region where solutions of hydrated salts in general are much more transparent than the pure solvent. This is clearly shown in both series of measurements given in table 12. Here we have employed a deeper layer of solution than in the series from which the curve for the 1μ band was plotted. Consequently, the intensity of absorption is greater, and this would have the effect of making more pronounced any peculiarity shown by a more shallow layer. The curves for the solution and solvent cross at a point closer to the violet end of the spectrum when deeper layers are used. This is evident from data given in table 12, and the results clearly show that the solution would not have the greater transparency at the center of the 1.25μ band.

The 1.25μ band (fig. 14) does not show any special peculiarities, there being several other bands of very similar character in the cases of the other hydrated salts. As might be expected from the nature of the results for the 1μ band, the solution is less transparent just before the center of the band is reached.

The transmission curves for ammonium bromide (figs. 15 and 16), being so widely different from those of the solvent, have been plotted to bring out the differences in general between hydrated and non-hydrated salts. Ammonium bromide is a typical non-hydrated salt, and the results for this salt can be compared with those for magnesium bromide, a typical hydrated salt.

In every case thus far studied, the solution of a non-hydrated salt is less transparent at the center of the band than the solvent. The differences in the case of ammonium bromide are quite marked. It is only through a narrow range of wave-lengths (that is, from 1.16μ to 1.18μ, fig. 13) that the solution is the more transparent in the neighborhood of the 1μ band, and even here the difference is very slight.

Near 1.2μ, where the hydrated salts are much more transparent than the solvent, ammonium bromide is about 30 per cent less transparent.

The curve for the 1.25μ band (fig. 16) brings out exactly the same relations as have been noted for the 1μ band. These curves cross in two places, as would be expected; first, in the region already mentioned for the 1μ band; second, for a small region around 1.3μ. For all other wave-lengths the solution is less transparent than the solvent.

Sodium nitrate gave results of a slightly different character from any that had been obtained for non-hydrated salts. The measurements were repeated three times, two series of results being recorded. In every case new solutions were used, yet results of the same general

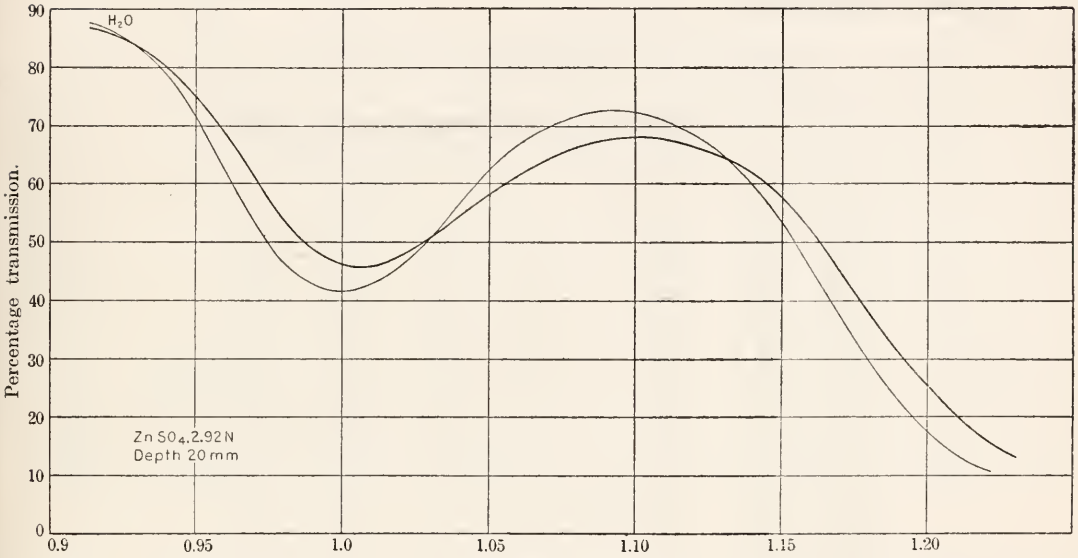

FIG. 7.—Wave-lengths.

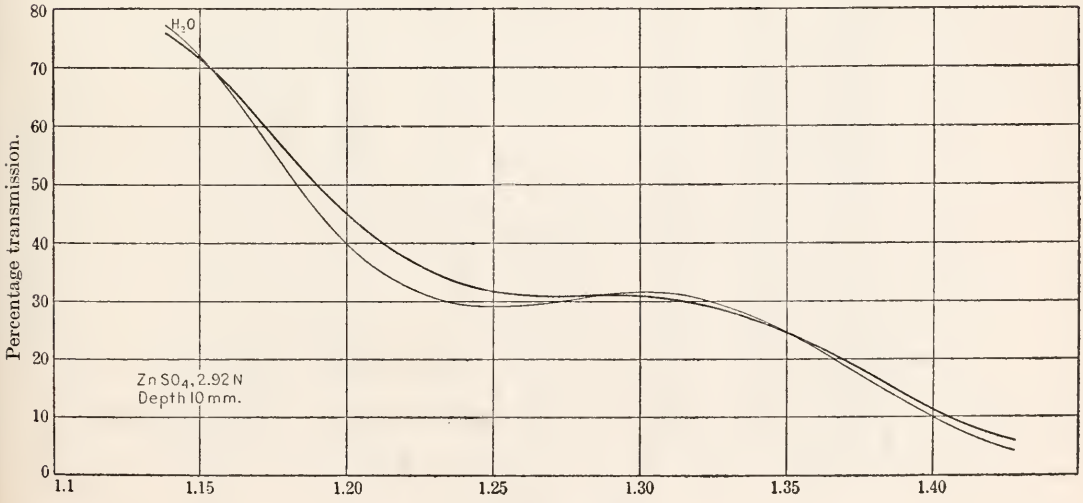

FIG. 8.—Wave-lengths.

character were obtained in each series of measurements. The curves for sodium nitrate (figs. 17 and 18) were plotted from the results given in column 5, tables 12 and 13.

The solution of sodium nitrate, as is the case with all the other non-hydrated salts, is less transparent than the solvent at the center of both bands. The difference is quite marked for this salt. The solution curve for both bands is very much more elongated than that for the solvent. At the point of maximum absorption it shows the greater absorption, and at the point of maximum transparency the greater transparency.

TABLE 12.—*Magnesium nitrate, ammonium bromide and sodium nitrate.*

λ	H_2O	$Mg(NO_3)_2$ 3.68 N.	$(MgNO_3)_2$ 3.63 N.	NH_4Br 4.016 N.	$NaNO_3$ 5.69 N.	$NaNO_3$ 4.95 N.
709	96.3	96.5	96.4	95.6	96.6	96.3
709	96.3	96.5	96.4	95.8	96.6	96.3
890	90.8	89.8	90.0	88.0	93.6	87.8
918	88.0	87.3	86.8	84.8	88.3	88.2
934	85.0	83.7	84.0	81.5	84.6	85.6
946	79.2	80.0	79.6	76.8	78.7	79.8
952	75.4	76.7	76.0	73.2	74.7	76.3
957	70.2	72.2	71.2	69.6	68.7	71.5
963	64.5	67.3	66.4	58.7	63.0	64.5
977	53.5	54.3	53.5	50.7	50 4	51.0
983	49.5	47.8	47.3	44.8	45.5	44.1
989	46.8	42.7	42.7	40.3	41.7	39.7
995	44.7	39.6	39.3	38.6	39.0	37.3
1002	44.0	38.5	38.5	37.0	38.9	36.4
1008	44.8	38 7	39.1	37.0	40.0	37.5
1008	44.7	39.2	38.6	37.7	39.9	36.2
1014	46.2	40.8	41.0	38.4	41.7	39.6
1022	47.8	43.6	43.3	40.3	45 0	42.0
1027	49.7	46.3	47.0	43.3	49.2	46.4
1035	52.7	50.0	50.6	46.1	52.8	51.2
1042	56.2	54.2	54.2	49.2	56.8	55.2
1048	59.5	57.7	58.5	52.6	60.9	59.4
1060	65.3	64.5	64.5	58.2	68.2	67.3
1073	70.6	68.6	69.6	62.8	73.9	73.8
1088	73.5	72.8	72.7	63.6	77.2	77.7
1103	75.2	74.7	73.4	65.5	77.3	78.2
1118	73.3	73.3	71.8	65.6	75.2	78.2
1132	70.7	70.2	69.5	63.3	71.6	73.7
1139	67.5	68.9	67.0	61.4	68.3	71.3
1147	64.0	65.7	64.3	60.3	64.3	67.7
1154	58.9	62.2	62.0	57.2	59.2	64.4
1162	53 0	58.2	56.4	53.5	53.4	58.4
1170	47.2	52.7	52.7	48.1	46.7	52.7
1177	41.2	44.7	44.5	41.2	40.3	44.5
1186	35.2	36.9	35.2	33.1	33.5	34.8
1195	29.7	28.8	28.7	25.4	28.2	26.4
1203	24.3	21.9	21.0	18.4	22.2	18.5
1210	19.8	15.9	16.5	13.5	17.4	12.8
1220	16.0	12.6	12.5	10.0	13.9	9.6
1227	13.5	11.0	10.1	....	11.2	8.5

DISCUSSION OF THE RESULTS.

The chief points of interest brought out by a study of the transmission curves for hydrated and for non-hydrated salts are the following: Aqueous solutions of hydrated salts generally have greater transparency than pure water at the centers of the absorption bands. The exceptions are the 1μ band for zinc nitrate (fig. 9) and magnesium

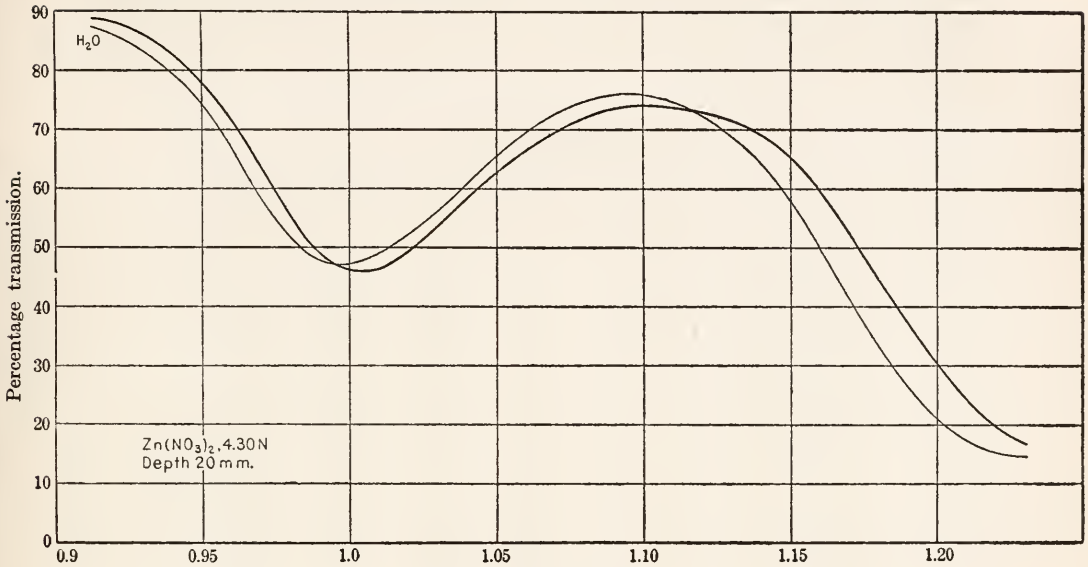

FIG. 9.—Wave-lengths.

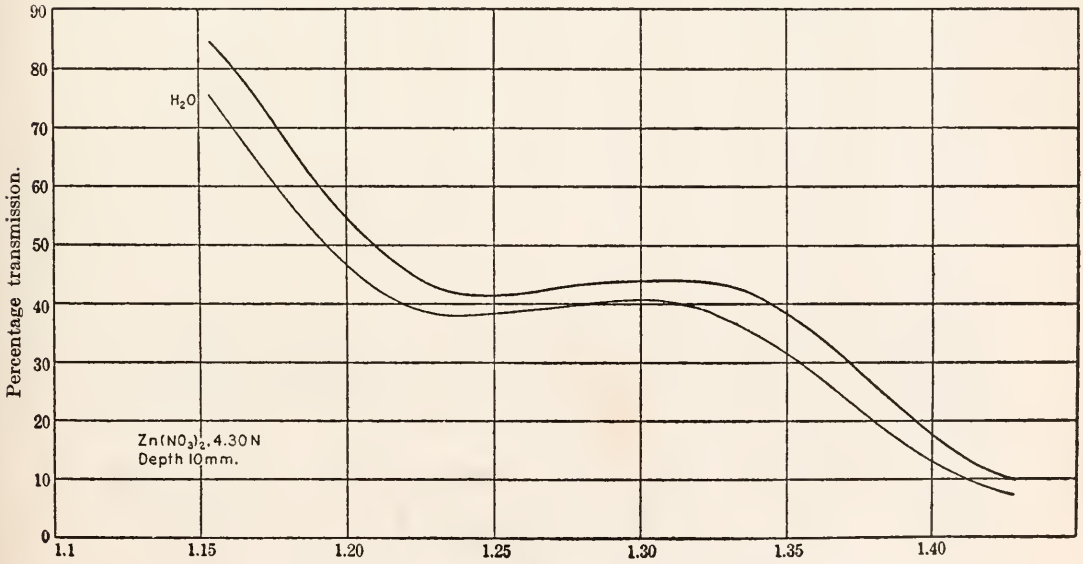

FIG. 10.—Wave-lengths.

nitrate (fig. 13) and the 1.25μ band for magnesium nitrate (fig. 14). The above relation is shown very clearly in many cases by a study of the curves for hydrated salts. With increasing wave-lengths, as the regions of intense absorption are approached the solution is much more transparent than the solvent. Near 1.2μ, as we approach the 1.25μ band, having in the path of the light 20 mm. of the solution, the solution is usually from 20 to 40 per cent more transparent than the pure solvent. This difference increases as the depth of the solution in the path of the light increases. It is very much less for 10 mm. of solution

TABLE 13.—*Magnesium nitrate, ammonium bromide and sodium nitrate.*

λ	H_2O.	$Mg(NO_3)_2$ 3.68 N.	$Mg(NO_3)_2$ 3.63 N.	NH_4Br 4.016 N.	$NaNO_3$ 5.69 N.	$NaNO_3$ 4.95 N.
709	98.5	98.3	98.0	98.0	98.5	98.0
709	98.5	98.3	98.0	98.0	98.5	98.3
1147	78.5	82.8	82.7	78.3	79.0	82.5
1154	75.2	80.4	80.3	76.2	75.5	80.0
1162	70.6	77.1	77.0	73.3	70.7	76.5
1170	65.0	72.9	72.7	69.2	64.8	72.3
1177	59.7	67.0	66.4	63.4	59.7	64.0
1186	54.5	59.4	59.4	55.7	52.7	56.2
1195	49.0	52.2	52.0	48.6	47.7	47.5
1203	44.7	44.7	44.7	41.6	42.3	40.1
1210	40.0	39.7	39.0	35.6	37.5	33.9
1220	37.2	35.8	34.5	31.8	34.2	30.6
1227	33.8	33.6	33.0	29.4	32.0	28.9
1235	33.4	33.4	32.7	28.2	30.8	29.0
1242	33.3	33.5	33.0	27.4	30.4	29.2
1250	33.1	33.9	33.1	27.7	31.6	30.4
1258	33.2	34.7	33.6	27.8	31.2	30.4
1258	33.4	34.5	33.6	28.1	31.2	30.6
1266	33.6	35.6	34.3	28.2	33.6	32.1
1272	34.0	36.3	35.0	28.8	34.6	33.6
1289	34.8	37.6	36.9	30.0	36.8	36.8
1303	35.4	39.3	38.2	31.1	38.6	38.3
1318	35.0	39.3	38.6	31.9	38.7	40.0
1331	33.4	38.2	38.4	31.7	37.2	39.5
1345	30.7	36.0	36.2	30.0	34.7	37.4
1359	25.8	31.2	31.5	27.0	29.7	31.9
1373	21.8	25.0	26.3	21.8	24.6	25.1
1386	16.7	19.0	21.0	16.5	19.2	19.5
1399	15.3	12.7	14.1	11.5	15.2	12.6

than for 20 mm., for the same wave-length of light. It requires an intense absorption to bring out these differences in a pronounced manner. A decrease in the concentration of the solution also decreases the difference between the absorption for the solution and for the solvent, as has been pointed out by Jones and Guy.[1]

Non-hydrated salts, under similar conditions, give results in many respects exactly the opposite of those obtained with hydrated salts. Three non-hydrated salts were investigated, and in all three cases the

[1]Carnegie Inst. Wash. Pub. No. 190, page 49.

solution had greater absorption than the solvent at the centers of the bands. In the previous work in this field, by Jones and Guy,[1] two other non-hydrated salts were studied (ammonium chloride and ammonium nitrate), and these showed exactly the same phenomenon. It will be remembered that for hydrated salts the solution was more transparent in all cases except the nitrates. The transmissions for the solution of potassium chloride are very nearly identical with those of water in the

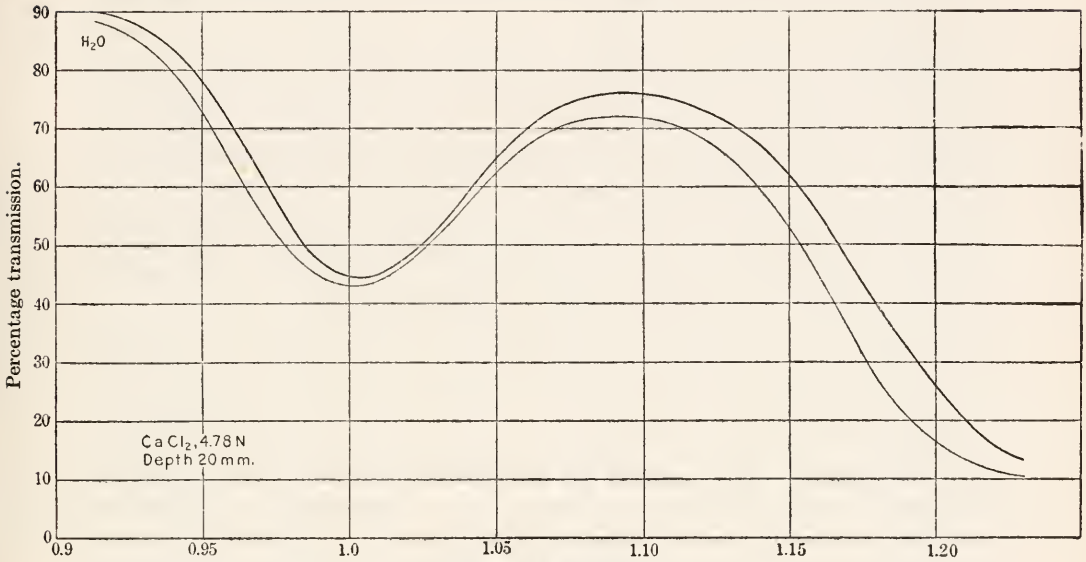

FIG. 11.—Wave-lengths.

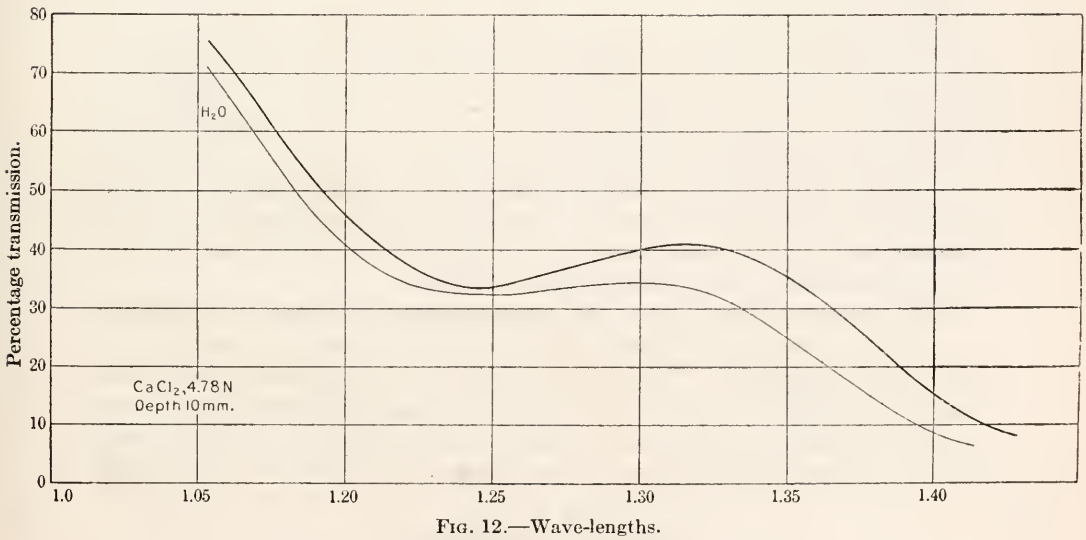

FIG. 12.—Wave-lengths.

[1]Carnegie Inst. Wash. Pub. No. 190; Phys. Zeit., **14**, 279 (1913).

case of the 1μ band, table 6; therefore, no curve was plotted for this salt. The results for the 1.25μ band, table 7, show differences between the absorption of the solution and of the solvent. The solution has the greater absorption at the center of this band, which is in accord with the results in general for non-hydrated salts. Otherwise the results are of the same general character as those for a very weakly hydrated salt.

The curves for ammonium bromide and sodium nitrate (figs. 17 and 18) present several new features. One of these makes it necessary to modify the statement[1] that solutions of non-hydrated salts have practically the same absorption as that of a layer of water equal in depth to the water in the solution. This is nearly true for potassium chloride, but not so for the two salts ammonium bromide and sodium nitrate. In all four of the curves expressing the relations between the transmissions of the solutions and of the solvent, as we approach and pass through the centers of the bands, the solution is much less transparent than the pure solvent. This is exactly opposite to the effect noted in the case of hydrated salts. Regions of the spectrum which, in the case of hydrated salts, showed that the solution was as much as 30 to 40 per cent more transparent than the solvent, show in the cases of both ammonium bromide and sodium nitrate, that the solution is 30 to 40 per cent less transparent. In both of these cases, however, a slightly deeper layer of solution was used than in the case of strongly hydrated salts. The 1μ band for ammonium bromide (fig. 15) shows that the solution is less transparent than the solvent. It will be recalled that with calcium chloride (figs. 11 and 12) a typical hydrated salt, the solution had the greater transparency for every wave-length of light investigated.

There seems to be fairly good evidence that there is a shift in some of the absorption bands. If there is any shift of the solution band for a hydrated salt, it is towards the red. The 1μ bands for magnesium chloride (fig. 1), magnesium nitrate (fig. 13), and zinc nitrate (fig. 9) are displaced slightly towards the red, and the centers of both bands for sodium nitrate (figs. 17 and 18) seem to be shoved slightly towards the violet end of the spectrum. There does not seem to be any justification for stating that there is a shift in either direction for any absorption band of any of the other solutions.

The question arises, why are concentrated solutions of hydrated salts more transparent than a layer of water equal in depth to the water in the solution? The answer involves, in our opinion, the solvate theory of solution. From earlier work[2] done in this laboratory, it was calculated that in a solution of magnesium chloride of the concentration 2.3 normal, about 65 per cent of the water present is at ordinary

[1]Phys. Zeit., **15**, 447 (1914).
[2]Carnegie Inst. Wash. Pub. No. 60.

temperatures combined with the dissolved substance. Only 35 per cent of all the water present is, therefore, acting as solvent water.

All of the solutions which we studied were of much greater concentration than the above. Since the total amount of water combined with the dissolved substance increases with the concentration of the solution, the percentage of combined water was greater than 65 in the solutions with which we worked. It has been pointed out that only 4

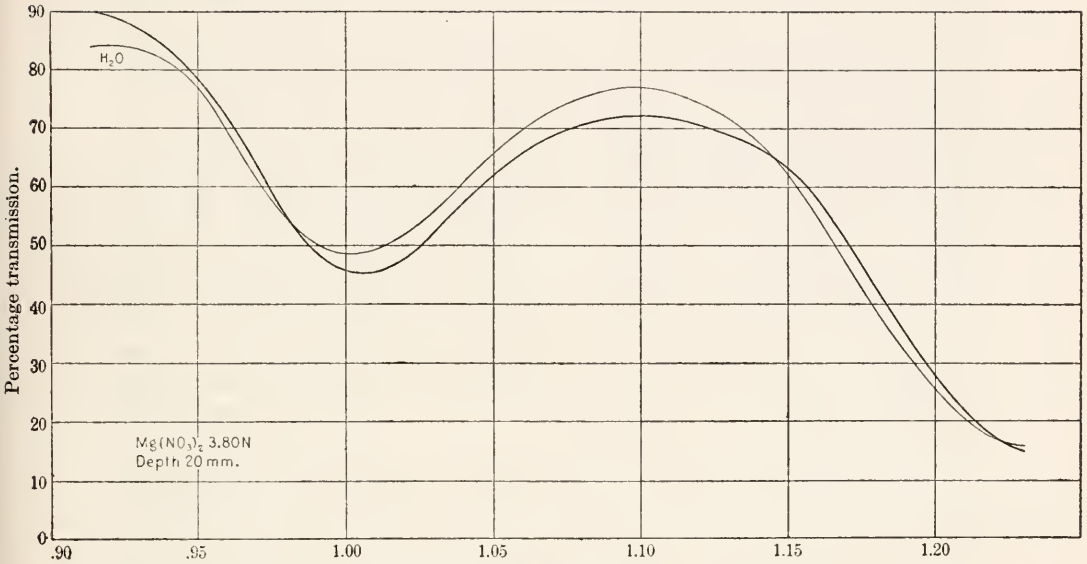

FIG. 13.—Wave-lengths.

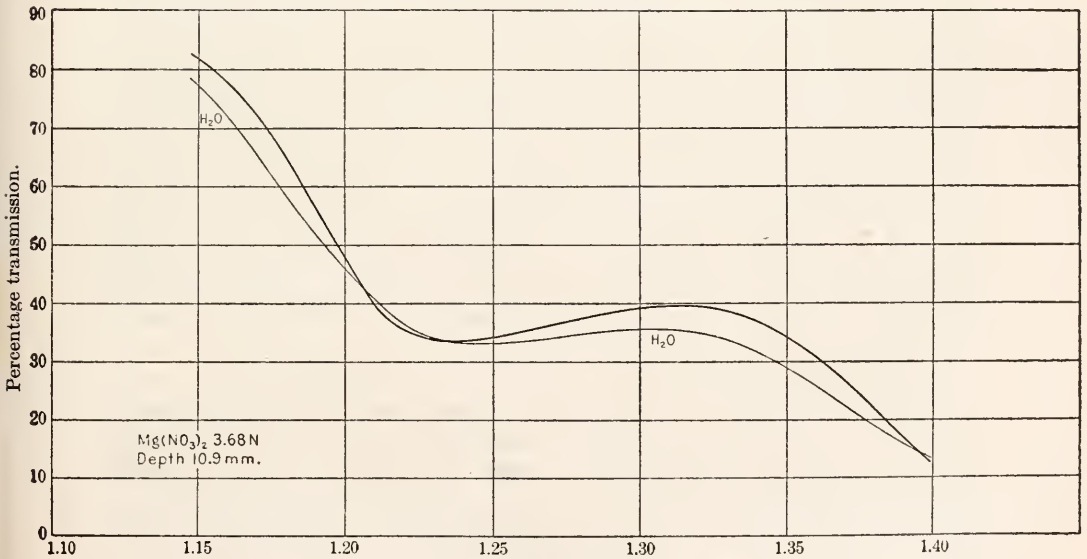

FIG. 14.—Wave-lengths.

of the 14 solution-curves given for hydrated salts show clean-cut evidence of a shift toward the red. This would, of course, cause the solution to be less opaque as we pass into and through the centers of the bands, and more opaque as we pass out of the bands and reach the points of greatest transmission. It is difficult to explain why the 1μ solution bands for magnesium nitrate and zinc nitrate (figs. 9 and 13) are more opaque at the centers of the bands, especially as there is fairly good evidence that a shift towards the red has taken place. The nitrates have a widely different molecular volume from any of the other salts studied. Their molecular volumes are very large. This may in some way account for the peculiarities in the transmission curves of the nitrates. The sulphates have small molecular volumes and in some manner produce a concentration in the solvent. The transmissions at the centers of the 1μ bands for solutions of zinc and magnesium sulphates are much higher than for any of the other salts studied by us (figs. 5 and 7). Solutions of sodium nitrate show that the nitrates probably have a freer vibrating system than even the pure solvent. Solutions of this salt show at the centers of both bands greater absorption, and at the tops of the bands higher transmission than the pure solvent. More attention should be given, in work of this character, to the volumes and masses of the vibrating systems, which undoubtedly vary widely with the addition of different salts.

It has been seen that in only 4 out of 14 curves for the hydrated salts is there any evidence of a shift of the solution curve towards the red. In our opinion the chief factor which makes the aqueous solution more transparent than a depth of water equal to the water in the solution is that hydration exists in the solution. It is quite certain now that in the solutions which we studied, much more than half of the water was combined with the dissolved substance. It seems almost a necessity that this would alter the vibrational frequency of the absorbing electrons or systems. The character of the transmission curves seems to justify the conclusion that water of hydration has less power to absorb light than pure uncombined water. We can conceive of no other rational explanation which will interpret satisfactorily our results for hydrated salts. That water of hydration is less opaque to light than free water seems, from our work, fairly certain. In this way alone is it possible for us to explain satisfactorily the transmission curves for hydrated salts.

A question of importance is why, for non-hydrated salts, is the transmission curve for the solution always below the transmission curve for the solvent, not only at the centers of the bands, but for most of the regions of the spectra which we studied? This is exactly the reverse of the relations already pointed out for the hydrated salts. Just before the centers of the bands are reached, passing in the directions of the longer wave-lengths, the solution of the non-hydrated salt

is as much as 35 per cent more opaque than the solvent. At present we can only conjecture as to the real cause of this effect. A shift towards the violet would make the solution more opaque at the centers of the bands; and although there is slight evidence of a shift in that direction for the bands of sodium nitrate, it is not at all apparent in the other bands. The curves do not bring out the characteristics in general which would be expected if the solution bands were displaced

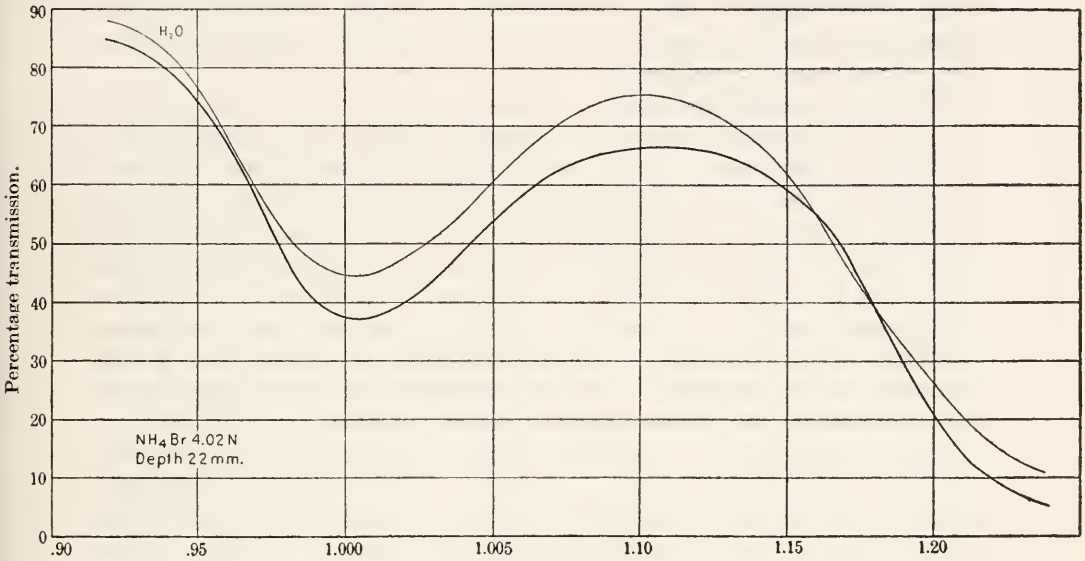

FIG. 15.—Wave-lengths.

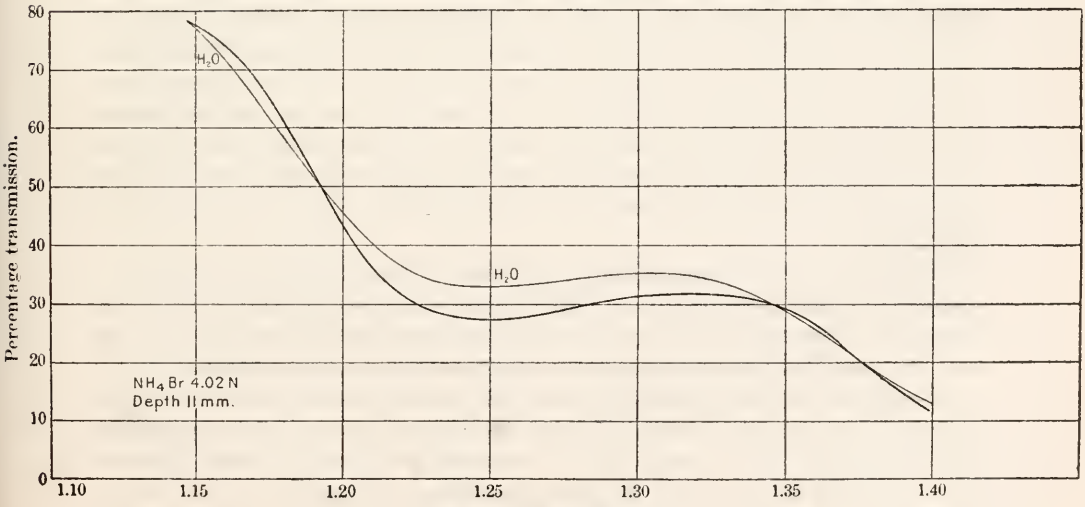

FIG. 16.—Wave-lengths.

towards the violet. Some other assumption of a more fundamental character is necessary to explain the phenomenon under consideration.

If the non-hydrated salts decreased the association of the solvent, and thereby produced an absorbing system freer to vibrate, it seems that most of the points brought out by the transmission curves could be satisfactorily explained. We should then expect the solution to be more opaque than the solvent at the centers of the bands. In case there was no shift in the bands, the same relations should hold for the other wave-lengths of light investigated. The above suggestion is at present to be accepted only tentatively, as offering a possible explanation of the results obtained.

We are now applying a method which we hope will decide whether the above assumption is or is not correct, whether the presence of a non-hydrated salt does or does not diminish the association of water.

Frequent reference has been made to the peculiar characteristics of the transmission curves for magnesium nitrate. It was desired to see whether the salt itself had any absorption. Some magnesium nitrate was prepared nearly anhydrous by repeated crystallization from absolute alcohol, and the salt was then dried in a vacuum over phosphorus pentoxide for several days. It was dissolved in acetone and a 1.07 normal solution prepared. This was studied spectroscopically in the same manner as has already been outlined for aqueous solutions.

Fifteen millimeters of acetone showed a faint band at 0.9μ, having less than 10 per cent absorption. Another quite similar band appeared at 1.03μ, part of which was probably due to water. At 1.22μ there is a fairly intense band absorbing about 60 per cent of the light. The absorption again reaches a maximum close to the point in the spectrum where our measurements for the 1.25μ water-band ended. Using such depths of the solutions that they contained as much of the solvent as had been employed to obtain the transmission of 15 mm. of the pure solvent, it was hoped, if magnesium nitrate did have any absorption of its own, that it could be detected. From 0.7μ to 1.3μ, which covers most of the spectrum studied in this work, the percentage transmissions for both the solution and the solvent were very nearly the same. There was, therefore, no indication of any absorption due to the dissolved substance.

Beyond 1.3μ, as we approached another intense band, some very unusual differences were noted. Until more work can be done with pure acetone in this region, and with anhydrous magnesium nitrate, we do not feel justified in drawing any conclusion from these results.

Anhydrous magnesium nitrate was also dissolved in some very carefully prepared absolute ethyl alcohol, the concentration of the solution being 0.53 normal. It was desired to learn whether the same kind of results would be obtained as had manifested themselves with water as the solvent. Table 14 is for 20 mm. of alcohol. It will be noticed

that the character of the transmission curve for alcohol is very similar to that for water.

Such depths of solutions were used that they contained in the one cell 21 mm. of alcohol and in the other 1 mm. As with acetone, the percentage transmissions for both the solution and the solvent are very nearly the same. This was perhaps to be expected, since with water the percentage transmissions of both solution and solvent are very

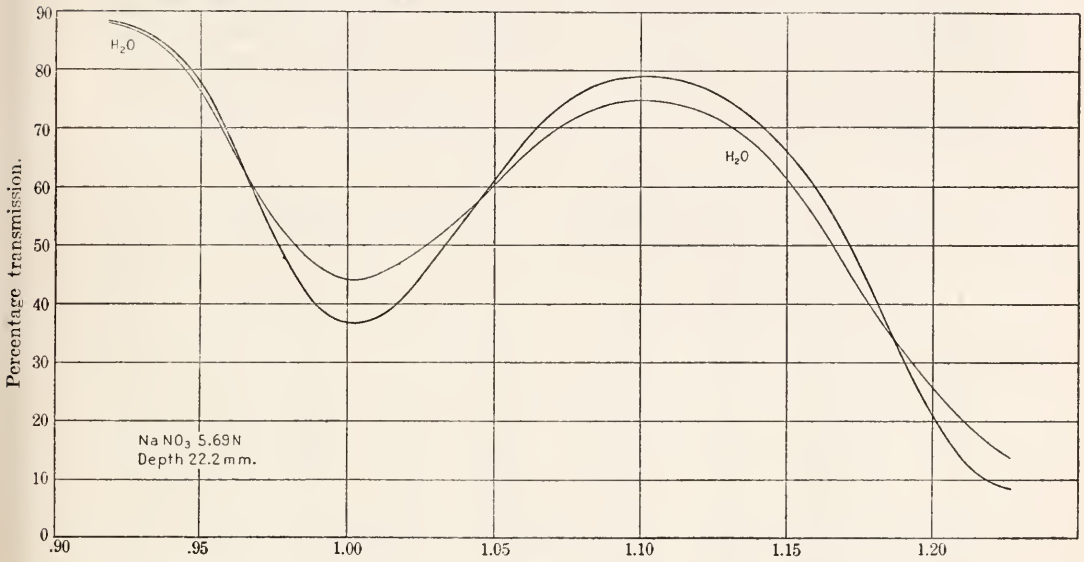

FIG. 17.—Wave-lengths.

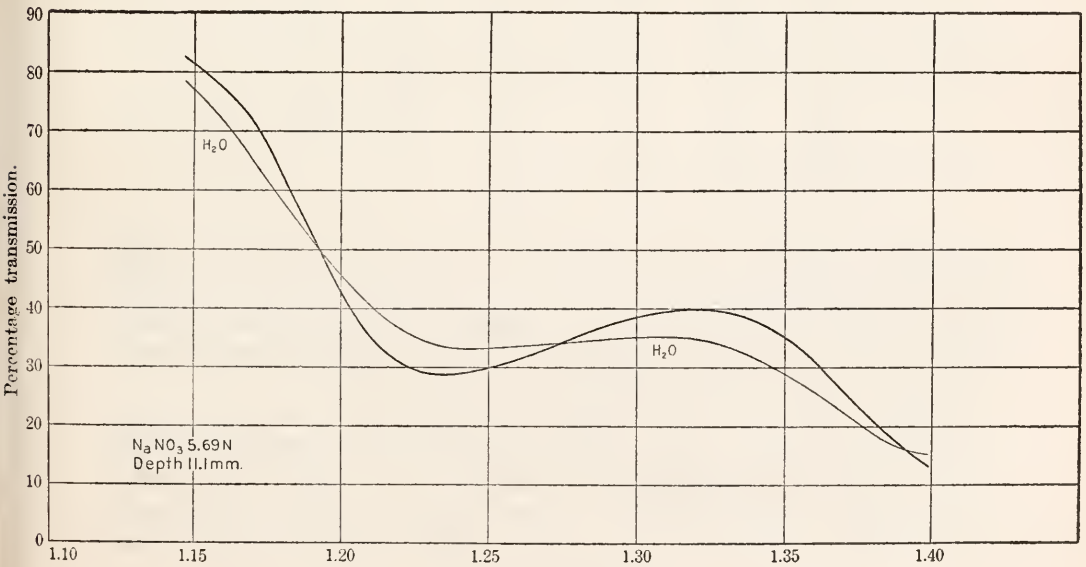

FIG. 18.—Wave-lengths.

nearly identical. The solution whose percentage transmissions are given in table 14, along with those of the solvent, is not nearly so strongly alcoholated as it would be hydrated at the same concentration if water was used as the solvent. Neither the work on magnesium nitrate in acetone, nor in absolute alcohol, presents any evidence that the salt has any absorption for the wave-lengths of light in question.

Jones and Anderson[1] and Jones and Strong,[2] in mapping and studying the absorption spectra of solutions, found abundant evidence for the existence of "solvent bands." In mixtures of certain solvents, say alcohol and water, neodymium salts showed simultaneously upon the plate two separate and distinct sets of absorption bands, where only

TABLE 14.—*Magnesium nitrate in alcohol.*

λ	C_2H_5OH	$Mg(NO_3)_2$ 0.53 N. in C_2H_5OH.	λ	C_2H_5OH	$Mg(NO_3)_2$ 0.53 N. in C_2H_5OH.
709	98.0	98 0	1118	79.0	81.0
709	98.0	98.0	1132	81.0	81.8
490	92.3	93.0	1147	80.0	77.3
907	88.3	88.7	1162	75.0	65.8
918	79.6	80.5	1177	62.4	49.3
934	81.5	81.4	1195	47.7	34.0
946	83.2	83.1	1210	32.6	20.8
957	85.0	85.3	1227	19.8	16.3
970	86.3	87.3	1235	15.5	13.5
983	85.5	86.6	1242	13.5	13.1
995	82.0	85.2	1250	13.5	14.0
1008	79.5	83.6	1258	15.3	16.7
1008	79.0	82.5	1266	18.2	19.6
1014	76.8	80.3	1272	21.6	27.3
1022	75.0	78.0	1289	29.2	36.0
1027	73.8	76.3	1303	36.7	43.4
1035	72.5	74.7	1318	43.3	50.0
1042	71.5	73.5	1331	47.0	53.6
1048	72.6	73.5	1345	49.7	54.9
1060	73.5	75.3	1373	49.2	41.7
1073	75.8	76.4	1399	35.7	21.5
1088	76.0	77.4	1426	15.6	....
1103	78.0	78.0			

one would appear in each solvent. They ascribed the one band to the hydrate formed with the neodymium salt and water, and the other to the alcoholate formed by the neodymium salt. The "water" band and the "alcohol" band appeared to be of equal intensity when 7 or 8 per cent of water was present in the alcohol.

A large number of other solvents were used, and "solvent" bands were found for each of them. They could even distinguish between a given alcohol and its isomer, by means of the absorption spectra of a neodymium salt dissolved in them. This was regarded as good

[1]Carnegie Inst. Wash. Pub. No. 110. *Ibid.*, Pubs. Nos. 130 and 160.

evidence that the neodymium salts were solvated. The photographic results were hardly more than qualitative. It was desired to study these "solvent" bands quantitatively.

The photographic work was done with a grating which gave considerable dispersion. It was hardly to be expected that the prism in the prism spectroscope which we used would disperse the light sufficiently to enable us to study the two "solvent" bands. We could, however, by means of the prism spectroscope and radiomicrometer, learn something of the difference in position and intensities of the "solvent" bands, and at least gain an idea as to how to proceed when, in the near future, we shall study this problem in detail with a large new grating spectroscope now completed, and with a still more improved radiomicrometer.

Seven solutions were prepared, each containing neodymium chloride of the concentration 0.141 normal. The two solvents were water and absolute ethyl alcohol. As recorded in table 15, the solvents contained the following amounts of water: 100, 50, 25, 13, 9, 3, and 0 per cent.

The neodymium chloride was of course dehydrated. This was effected by heating for a long time at about 150° in a current of dry hydrochloric-acid gas. All the solutions used were perfectly clear. The depth of layer employed in determining the percentage transmissions for each solution was 10 mm. The results recorded in the table enable us to study three neodymium bands for each solution. It is evident that the greatest changes in the percentage transmissions take place in those solutions which contain more than 90 per cent alcohol. The bands for only three of the solutions have been plotted (fig. 19). They are the bands for neodymium chloride in 100 per cent water, in 97 per cent alcohol, and 100 per cent alcohol. The heavy curve nearest the violet end of the spectrum is for 100 per cent water. The dotted curve is for 97 per cent alcohol, while the curve represented by dashes is for 100 per cent alcohol.

It is evident that the spectrum does not show any indications of a hydrate and an alcoholate band, both bands appearing as one. This was anticipated, since the dispersive power of the glass prism is so slight. Near the centers of the bands, on both the descending and ascending arms and at the center of the bands, the wave-lengths of light recorded in the table are those which would be obtained by turning the calibrated head of the spectrometer one division. This increased or decreased the wave-lengths of light through this region by about 40 A. U., according to the direction in which the drum-head was turned. Increasing the wave-length to this extent would make it impossible to detect the two "solvent" bands. Accordingly, the drum-head was turned through increments of about 5 A. U. and the transmission determined. This was done for the mixed solvents for all three bands given in the curves, and also for a few of the bands which showed best the

"solvent" bands when the photographic method was employed. Working in this way, even with the small dispersion of the glass prism, fairly definite indications were obtained of the existence of "hydrate" and "alcoholate" bands. It will, however, be necessary to use a spectroscope with higher resolving power to bring out more clearly the existence of "solvent" bands. Such a piece of apparatus is now completed.

The curves in figure 19 present many interesting features. The intensity of absorption for neodymium chloride in 100 per cent water is much greater than that for neodymium chloride in 100 per cent alcohol. It can be stated, in general, that the intensity of the absorp-

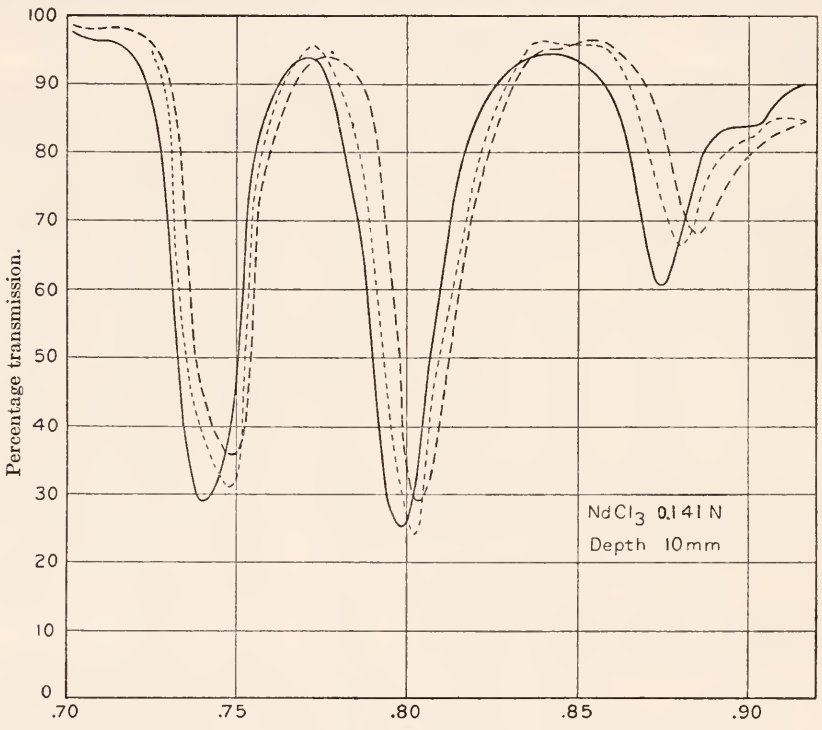

FIG. 19.—Wave-lengths.

tion increases as the water-content increases. Neodymium chloride in water has a band whose center is at $\lambda = 0.739\mu$, and here the percentage transmission is about 29. For neodymium chloride in alcohol it is nearly 50 per cent for the above wave-length. The transmission of neodymium chloride in water for this wave-length of light is therefore about 40 per cent less than the transmission for this same salt in pure alcohol. The ratio of intensities of the hydrate and of the alcoholate bands is about the same at 0.8μ, where the center of the second band for neodymium chloride in water is located. The much less intense neodymium water-band, whose center is at $\lambda = 0.875\mu$, is barely 30 per

cent more intense than that for neodymium chloride in pure alcohol. On the ascending arms of the curves exactly the opposite effects are noted. This indicates a displacement of the alcoholate band to the region of longer wave-lengths. The displacement is very large in the case of the first band. Neodymium chloride in 100 per cent water has a band whose center is at $\lambda = 0.739\mu$. When the solvent is 100 per

TABLE 15.—*Results for neodymium chloride in mixed solvents. Concentration 0.141 normal.*

λ	100 p. ct. H_2O	50 p. ct. H_2O	25 p. ct. H_2O	13 p. ct. H_2O	9 p. ct. H_2O	3 p. ct. H_2O	0 p. ct. H_2O
702	97.7	98.0	98.0	97.6	100.0	100.0	100.0
702	98.1	98.0	98.0	98.0	98.0	98.0	98.0
709	95.9	96.3	96.2	98.0	98.1	98.1	98.2
717	96.3	94.8	95.0	96.2	98.2	98.2	98.3
725	89.6	91.8	93.6	91.3	95.3	96.5	96.8
732	51.7	52.3	55.6	55.2	62.8	74.6	88.2
736	42.3	41.3	42.2	40.0	44.4	50.7	68.2
739	28.8	32.0	31.8	30.5	34.4	40.9	49.3
743	29.5	31.8	22.3	29.5	32.8	36.1	41.3
743	29.9	32.0	31.9	29.7	32.2	34.8	40.7
749	40.0	43.0	40.0	37.5	35.3	31.2	35.7
749	41.8	43.0	39.7	37.7	35.9	32.4	35.2
753	58.0	59.7	58.7	54.3	52.7	45.2	41.8
753	58.7	59.5	59.4	55.4	53.5	45.2	41.6
756	78.3	75.0	76.0	75.6	73.7	65.7	62.1
764	91.1	91.0	89.6	91.3	91.6	89.3	85.2
773	94.1	92.5	93.5	96.6	97.6	95.6	93.6
780	84.5	83.6	85.5	85.7	89.3	91.6	93.9
789	58.4	56.7	57.7	61.5	64.6	74.0	88.3
794	32.2	32.2	32.6	34.1	38.0	53.1	70.3
799	25.0	21.8	21.8	21.6	21.3	27.8	48.6
803	31.6	32.3	31.3	29.0	29.0	24.5	29.0
803	32.7	32.0	32.7	29.2	28.8	24.0	30.1
807	50.8	49.0	50.5	48.2	45.6	41.5	32.4
807	51.3	49.3	51.4	48.2	46.5	40.9	33.1
813	68.7	69 5	68.2	65.7	64.5	57.3	49.6
817	80.3	79.8	80.2	77.5	75.8	68.0	64.2
823	85.6	86.3	86.5	84.7	82.7	79.4	76.2
828	90.8	90.5	90.7	90.2	90.7	87.3	84.8
837	94.2	92.5	95.6	93.7	95.3	95.7	94.7
847	93.6	91.6	95.3	94.8	95.5	95.9	95.1
858	90.5	90.0	92.0	92.3	94.3	95.5	96.1
869	71.6	70.6	73.7	74.5	77.4	84.1	91.0
875	60.7	60.8	60.8	62.3	65.5	72.4	84.1
875	60.3	61.2	61.2	62.8	65.5	72.3	82.7
880	66.3	66.7	66.3	65.7	65.6	66.3	73.6
880	66.4	66.0	66.3	65.6	66.0	66.3	73.0
885	76.5	75.8	77.6	74.8	74.0	70.3	68.1
885	77.5	76.0	77.0	75.0	73.4	71.9	68.8
890	82.3	82.1	83.5	81.3	80.8	77.6	71.3
896	83.6	....	....	....	82.4	80.7	76.7
903	83.6	82.9	84.5	83.9	....	82.5	80.6
907	86.2	....	....	....	....	84.5	82.4
918	90.3	86.3	87.0	85.6	85.1	84.3	84.7
934	89.5	....	....	82.6	....	....	89.2
946	85.6	....	....	....	89.5	90.3	91.7

cent alcohol, the alcoholate band has its center at $\lambda = 0.749\mu$, the displacement here being about 100 A. U. For the second band the displacement is only about 40 A. U., while for the third it is over 100 A. U. When the percentage of alcohol is below 90, the bands for the mixed solvents are only slightly displaced towards the red, the greatest change taking place between 90 and 100 per cent alcohol.

Similar experiments were carried out with anhydrous neodymium chloride dissolved in pure glycerol and in water. The salt was also dissolved in mixtures of the two solvents. The glycerol bands were very slightly, if at all, displaced towards the longer wave-lengths.

It gives us pleasure to express our thanks to Professor H. A. Pfund and to Professor John A. Anderson, for many valuable suggestions during the progress of this work.

CHAPTER II.

CONDUCTIVITIES, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY, DISSOCIATIONS, AND CONSTANTS OF CERTAIN ORGANIC ACIDS IN AQUEOUS SOLUTIONS.

By Leslie D. Smith.

A part of Dr. Smith's work with the organic acids has already appeared in Publication No. 170 of the Carnegie Institution of Washington. The remainder of his work is included in this chapter.

INTRODUCTION.

This investigation is a continuation of work which has been in progress during the past 12 years on the conductivity, temperature coefficients of conductivity, and dissociation of electrolytes between 0° and 65°. The work was undertaken in connection with the solvate theory of solution, which was proposed by Jones about 15 years ago.

The first work was done by Jones and West[1] on certain salts, and extended over the temperature range 0° to 35°.

The second investigation was by Jones and Jacobson[2] on a number of salts, over the same range in temperature.

The work of White and Jones[3] was on the conductivity, dissociation, and dissociation constants of a number of organic acids from 0° to 35°.

The fourth investigation was by Clover and Jones,[4] using organic acids and salts. The conductivities were measured from 35° to 80°. This was the first piece of work done in this laboratory over the higher range in temperature.

The second piece of work of White and Jones[5] was on the conductivity, dissociation, and dissociation constants of a number of organic acids from 0° to 35°.

The second investigation of Jones and West[6] was on a number of salts between 35° and 65°.

The seventh investigation in this field was by Wightman and Jones,[7] on the conductivity, dissociation, and dissociation constants of organic acids between 0° and 35°.

The eighth, by Hosford and Jones,[8] had to do with the conductivities, temperature coefficients of conductivity, and dissociation of certain electrolytes from 0° to 35°.

The ninth, by Winston and Jones,[9] dealt with the conductivities, temperature coefficients of conductivity, and dissociation of certain salts from 0° to 35°. Miss Winston independently worked out an interesting theory of induction in solution.

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[1] Amer. Chem. Journ., **34**, 357 (1905).
[2] *Ibid.*, **49**, 355 (1908).
[3] *Ibid.*, **42**, 520 (1909).
[4] *Ibid.*, **43**, 187 (1910).
[5] *Ibid.*, **44**, 159 (1910).
[6] *Ibid.*, **44**, 508 (1910).
[7] *Ibid.*, **46**, 56 (1911).
[8] *Ibid.*, **46**, 240 (1911).
[9] *Ibid.*, **46**, 368 (1911).

The second investigation by Wightman and Jones[1] had to do with the conductivity and dissociation of certain organic acids from 35° to 65°.

The eleventh investigation in this field was by Springer and Jones,[2] on the conductivity, dissociation, and dissociation constants of a large number of organic acids between 0° and 65°.

The twelfth piece of work was done by Howard and Jones[3] on the conductivity, temperature coefficients of conductivity, and dissociation of certain electrolytes between 35° and 65°.

The thirteenth research was carried out by Shaeffer and Jones[4] on the conductivity, temperature coefficients of conductivity and dissociation of certain salts. They also studied the effect of hydration and hydrolysis. A number of salts which had presented apparent abnormalities in the earlier work were studied.

All of the above work, and that which was done by Smith over the temperature range 35° to 65°, has been discussed in Publication No. 170 of the Carnegie Institution of Washington.

The foregoing brief survey of the investigations in this laboratory is all that is necessary here, since the papers by White and Jones[5] and by Wightman and Jones,[6] already referred to, contain a careful review of the work previously done on the conductivity of organic acids in aqueous solution.

PURPOSE OF THE INVESTIGATION.

The object of this investigation was to secure more data concerning the dissociation of organic acids over a wide range in temperature and dilution, to improve methods, to test the work already done, and to discover new relations between the additional data obtained.

EXPERIMENTAL.

The investigation here discussed extended over about two years. The first year was devoted to a study of the conductivity and dissociation of certain organic acids at 35°, 50°, and 65°. The acids used were some of those that had been studied at the lower temperatures by other workers. The readings at 35° were repeated, and the agreements were very satisfactory. Where the difference was appreciable the work was repeated. If the difference was still too great to be due to unavoidable experimental error, the readings at the lower temperatures were taken again and a complete set of new data secured. The agreements were very close in practically every case, although the readings were taken by different investigators.

The work during the last year was devoted to the study of several acids at the lower temperatures, 0°, 12.5°, 25°, and 35°.

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[1] Amer. Chem. Journ., **48**, 320 (1912).
[2] *Ibid.*, **48**, 411 (1912).
[3] *Ibid.*, **48**, 501 (1912).
[4] *Ibid.*, **49**, 207 (1913).
[5] *Ibid.*, **44**, 156 (1910).
[6] *Ibid.*, **46**, 56 (1911).

The acids which had already been investigated by White and Jones at the lower temperatures, and which were reinvestigated by the author were, hippuric, gallic, picric, and crotonic. In every case very close agreements were found, and the values at 35° agreed to within the limits of experimental error. The temperatures were the same as those used by the former investigators.

REAGENTS.

The water used was purified in the same manner as that employed in the earlier investigations. This method was described in detail by Jones and Mackay.[1]

The acids were obtained from Kahlbaum and Schuchardt. The general method of purification was recrystallization from conductivity water. The butyric acids—normal and iso—were purified by distillation in a vacuum; acetaminobenzoic acid was recrystallized from ether.[2] Whenever possible the acids were carefully dried in a vacuum desiccator containing sulphuric acid. If practicable, the melting-points of the acids were taken as one criterion of purity. The "mother" solution, *i. e.*, the one with the greatest concentration, was made up whenever possible by direct weighing, and then titrated against standard alkali. The acids which are liquids were made up directly by titration. The modification of this method for the higher temperatures was described in detail in the paper by Wightman and Jones.[3] All flasks and burettes used in this investigation were calibrated by the method of Morse and Blalock,[4] and also by weight of the contained water.

The sodium salts of the organic acids were used to determine the μ_∞ values of the acids, and were prepared by titration. It had been found that the sodium salts of organic acids, in general, are completely dissociated at a dilution of $V = 2048$. Therefore, a solution of the acid at this dilution was just neutralized by sodium hydroxide, using phenolphthalein as the indicator, and its conductivity determined in the usual way.

APPARATUS.

The cells used in this investigation were the same as those employed by Jones and Wightman. In their paper they state:[5]

"The cells resembled those used by Jones and Bingham,[6] with platinum-plate electrodes attached to glass tubes containing mercury, the tubes being sealed into ground glass stoppers. As many as eight cells were employed with constants ranging from about 10 to 330 in Siemens units. A cell of special type,[7] having a very low constant, was used for obtaining the conductivity of the water. In order to get a sharp reading in the cells, the electrodes were covered with a fine coating of platinum black, in the usual manner."

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[1] Amer. Chem. Journ., **19**, 91 (1897).
[2] Carnegie Inst. Wash. Pub. No. 170.
[3] Amer. Chem. Journ., **48**, 320 (1912).
[4] *Ibid.*, **16**, 479 (1894).
[5] *Ibid.*, **46**, 62 (1911).
[6] *Ibid.*, **34**, 493 (1905).
[7] *Ibid.*, **45**, 282 (1911).

The thermometers employed were carefully compared with a standard Reichsanstalt thermometer. The standard thermometer was also calibrated at the United States Bureau of Standards.

The resistance box which was used throughout this entire investigation had also been calibrated by the Bureau of Standards. A very fine slide wire bridge was employed, the wire being wrapped around a marble drum. On this bridge the investigator could easily read to fractions of a millimeter. The entire scale was 5 meters long, and readings could be made to tenths of a millimeter.

The cells were kept at a constant temperature in thermostats. As this work was carried on simultaneously with that of Dr. Wightman, and partly using his apparatus, reference is made to his description of the system of thermal regulation. In the paper by Wightman and Jones[1] the system of regulation for temperatures 0° to 35° is fully described. They say:

"Three thermostats were employed to keep the cells at constant temperature; one for 0° similar to that described by Jones and Jacobson;[2] one for 15° (in this case for 12.5°) and 25°, a galvanized tub containing 20 to 30 liters of water, and in the bottom of which was placed a lead (in this investigation, copper) coil through which cold water was passed under constant pressure; a third for 35°, differing from the latter only in not having a coil in the bottom. They were both kept constantly stirred by propellers driven by a hot-air engine. In this way it was possible to keep the temperature constant to within 0.02°."

The work at the more elevated temperatures was carried out in apparatus similar to that used at the lower temperature, with the difference that the thermostats were covered with asbestos boards saturated with paraffin. The thermometer and stirrer passed through small openings in the cover, and the cells were placed in the bath through openings just large enough to admit them. These holes were covered by pieces of the same material as the cover. The evaporation of the water in the bath was in this way reduced to a minimum, and the confined vapors maintained the cells, both the exposed portion and the part immersed in the bath, at the same temperature. Thermoregulators of the same type as are used throughout this laboratory were employed.

There has been much less work done here at higher than at lower temperatures; therefore, a more detailed description of the various difficulties encountered, and the methods devised to overcome them, will be given.

The only work that had been previously carried out at the higher temperatures is that of Clover and Jones[3] and of West and Jones.[4]

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[1] Amer. Chem. Journ., **46**, 56 (1911).
[2] *Ibid.*, **40**, 355 (1908).
[3] *Ibid.*, **43**, 187 (1910).
[4] *Ibid.*, **44**, 508 (1911).

PROCEDURE.

The cell constants were taken by the method described by White and Jones.[1] When working at low temperatures they were determined as often as once a month, and still more frequently when working at high temperatures. The experimental difficulties are much more numerous at the higher than at the lower temperatures. There is a greater and more frequent variation in the cell constants. The solubility of the glass is often too large to be negligible. A few short quotations from the work of Clover and Jones, referred to above, will give the results of their investigations in the best possible forms.

CELL CONSTANTS.

"It has developed that a strain is brought about by the high temperatures which may result in a change either in the distance of the electrode plates from each other or in the surface of the plates. Since such a variation had not previously been observed in work covering a range of 0° to 35°, it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of 45° to 50°."

They performed an experiment to test the value of this method.

"The measurements were first carefully made at 35° and then duplicated; then the regular systematic procedure was gone through at 65°, and after this the readings at 35° were again made. If the results found the second time should agree with those first obtained at 35°, this would be strong evidence that the method was reliable. It was found in some cases that the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the concentration of the solution. It was further found that on standing for a considerable length of time at 35° (2 or 3 hours), *the reading slowly changed back in all cases to the original value.* It is difficult to see what other causes can be assigned to these results than a temporary change in the cell constant during the heating at 65°."

In conductivity work carried out at ordinary temperatures, experiments have shown that the error introduced by the solubility of the glass is negligible. However, at 50° the error from this same source at a dilution of one liter is the largest of all the ordinary experimental errors. The glass is still more soluble at 65°, as would be expected. Clover and Jones point out that at 80° the conductivity of pure water is increased tenfold on standing in the cells for a couple of hours. The cells used in their research were made of hard glass. Obviously, the amount of glass dissolved from the cells depends largely upon the nature of the glass of which the cells are made. It varies considerably with the different cells. The attempt to introduce directly a correction factor for the solubility of glass was therefore abandoned. This source of error was overcome in another way.

[1]Amer. Chem. Journ., **42**, 520 (1909).

It was found that after the cells had been heated with water for several hours, the amount of glass dissolved gradually decreased and finally became practically nothing. After this treatment, as the cells were kept in a bath at 45° and 65° and the water in them changed once a day, the solubility of the glass at 65° was always practically zero and therefore negligible. If a cell was removed from the bath and allowed to stand filled with water at room temperature for any appreciable length of time, it was found on heating that glass was again dissolved.

In this investigation the above precautions were all observed. In addition, at the start of the work the glass vessels were heated with a dilute solution of caustic soda, then boiled with dilute hydrochloric acid, and then for some time with conductivity water. The solubility of the glass was shown by tests to have been reduced to a negligible quantity by this treatment. The cells were then kept filled with conductivity water which was changed every day, and were maintained at a temperature approximately 50°, and thus the solubility of the glass was negligible. This was proved experimentally. A cell was filled with conductivity water at 35° and the conductivity read; then it was heated and readings were made at both 50° and 65°. The solution was cooled to 35° and the conductivity again measured. Since the two readings at 35° coincided, there was no appreciable quantity of glass dissolved during the process.

This was not the only beneficial result obtained from keeping the cells always at an elevated temperature. The expansion of glass and of platinum is not large enough to affect appreciably the cell constants, as would be the case if the temperature varied over a wider range.

It has already been stated that it takes several hours for a cell to acquire its normal condition at the lower temperature, with respect to the electrode-plates and the glass rods when suddenly cooled. This fact was utilized in the determination of the cell constants at the higher temperatures. The cells were kept at about 50°, and when the cell constants were to be taken the cells were filled with the solution of potassium chloride and they were heated to 50° for about an hour. The cells containing the solution were then cooled down and the conductivity read immediately after a constant temperature had been reached. The readings were made at 25°, where the conductivity of the solutions of potassium chloride is accurately known.

The method of White and Jones was used for taking the cell constants over the entire range of temperature from 0° to 65°.

Two objects were accomplished in all the work at higher temperatures, by filling the cells nearly to the top with the solutions. First, evaporation and the consequent change in concentration were reduced to a minimum. Second, carbon dioxide and other gases from the air were prevented from being present in sufficient quantity to affect the results.

The method of preparing the solutions was that devised by West and Jones:

"Since we worked over a range of temperature of only 30°, we found it convenient to prepare the solutions at the intermediate temperature, 50°, and then to use the solutions at the three temperatures, 35°, 50°, and 65°. But since the volume of a solution varies with the temperature, it was, of course, necessary to apply a correction at 35° and 65° to the volume of solutions made up to 50°.

"When a standard solution is cooled from 50° to 35° there is a contraction in volume and a consequent increase in the concentration of the solution. The value of μ_v for any solution would, therefore, be slightly too large. The value of μ_v as found must be multiplied by the factor 0.994 for results at 35° when the solutions were made up at 50°. The correction factor for solutions made up at 50° and used at 65° is 1.0076. The coefficient of expansion for distilled water is somewhat less than that for an aqueous solution. However, the difference in the coefficients for water and for that of our most concentrated solution is so small that it is negligible. By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved."

When Wightman, Springer, and Smith began the investigations at the higher temperatures the two problems presenting themselves were:

(1) In making up the solutions at 50° the glass of the flasks would dissolve, because the flasks were not kept at 50° in a bath, but, when not in use, were allowed to cool down to room temperature.

(2) The solution, even if heated to 50°, would cool off when poured into the burette, and still further when draining into the flask; therefore, instead of drawing off 50 c.c. of the solution at 50°, 50 c.c. would be drawn off at a temperature of $50°-x°$, or more than 50 c.c. at 50°.

This complex source of error was overcome by the above-named workers, all of whom started simultaneously the present line of work at elevated temperatures. The results are given in the paper by Springer and Jones:[1]

"A simple device did away with both of these sources of error. At 50°, 988.07 grams of distilled water have a volume of 1000 c.c. Our liter flask was weighed at 20°. Then 988.07 grams of distilled water at 20° were introduced—air displacement being taken into account. The flask was marked at the bottom of the meniscus. This flask, filled to the mark with water at 20° (room temperature), will contain a liter at 50°. Therefore, all the mother solutions could be made up for 50° work at 20°, and the solubility of the glass, which is noticeable only at higher temperatures, is thus made negligible. This mother solution will be, let us say, normal at 50°. At 20° it is stronger than normal. If we draw out 100 c.c. at 20° and dilute it to 200 c.c. at 20°, it will also be stronger than half-normal. But heat this latter solution to 50° and it will again attain its required normality—assuming that the coefficient of expansion of water is the same as that of dilute solutions. And all solutions worked with were eighth-normal, or more dilute. This permits the titration of all solutions at room temperature, which obviates the second of the above difficulties."

[1]Amer. Chem. Journ., **48**, 417 (1912).

This solution of the above-mentioned problems was worked out by Jones and Springer and Smith jointly, and with the same apparatus. We used a 500 c.c. or a 200 c.c. flask calibrated in this way for 50° at 20°, in which to make up our mother solutions. In the higher temperature work it was noted that bubbles of air formed on the electrodes, especially at 50° and 60°. These were removed by carefully shaking the cells before making the readings.

VALUES.

The values of the limiting conductivities of the monobasic acids were found directly from the μ_∞ values of their sodium salts. It has been shown by experiment that the conductivities of sodium salts, made up by the titration method, which, as already stated, was used in this work, agree with the conductivities of solutions which were made up directly from the dry, solid, sodium salt. The μ_∞ values of the acid

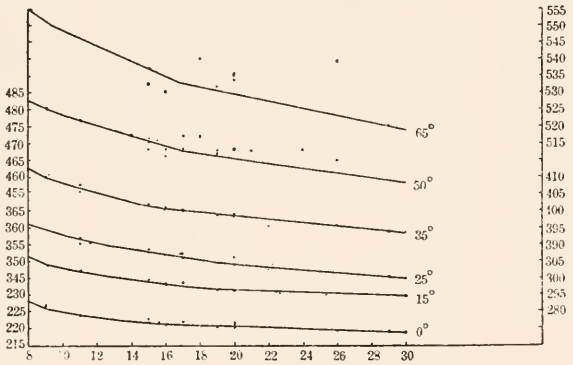

FIG. 20.—Limiting conductivities.

were obtained from those of the sodium salts by a very simple method. It consists in subtracting the constant of the sodium ion from the limiting conductivity value for the sodium salt, and then adding to this value the constant for the hydrogen ion. This may be readily accomplished in actual work by using this equation: μ_∞ acid = μ_∞ HCl+μ_∞ Na salt of acid − μ_∞ NaCl.

To calculate the value of μ_∞ for hydrochloric acid and sodium chloride at the various temperatures at which the work was done, the equations of White and Jones were used:

For sodium chloride, $\mu_\infty = 63.04 + 2.04\,t - 0.00823\,t^2$

For hydrochloric acid, $\mu_\infty = 245.4 + 6.06\,t - 0.00776\,t^2$

Table 16 gives all the values of the acids with which Smith worked. The μ_∞ values of dibasic acids could not be determined by this method. The sodium salts of dibasic acids do not yield a maximum value of conductivity at dilutions at which work could be done. Comparison of the μ_∞ values of the acids which Jones and several of his co-workers have studied, shows that those acids with the largest number of atoms

in the anions have the smallest μ_∞ values. A curve in which the ordinates represent the μ_∞ values of the acids, and abscissas the number of the atoms, was plotted for all these acids.[1] By placing the dibasic acids on this curve according to the number of atoms present, their values were obtained. (See fig. 20.)

The values for the acids marked with an asterisk (*) in table 16 were determined by other workers in this laboratory, and can be found in publication No. 170 of the Carnegie Institution of Washington, pages 91 and 92. It was shown that acids having the same number

TABLE 16.—*Limiting conductivities of the acids.*

Acid.	0°	12.5°	25°	35°	50°	65°
Butyric*	.....	.....	.....	404	473.3	540.3
Isobutyric*	.....	.....	.....	403	437.29	468.7
Malic	221.5	286.2	352	400	.....	.....
Pyrotartaric*	.....	.....	.....	397	468	533
Racemic*	.....	.....	.....	398	468.2	534.9
Hippuric	219	280	345	392	446.4	499.8
Citric*	.....	.....	.....	392	464.5	528.5
Aconitic	220.2	285	350	398	.....	.....
Crotonic	222	286	352	402	475.1	544
Maleic*	.....	.....	.....	402	475	544
Fumaric*	.....	.....	.....	402	475	544
Itaconic*	.....	.....	.....	400	471	537.5
Citraconic*	.....	.....	.....	400	471	537.5
Mesaconic*	.....	.....	.....	400	471	537.5
m-Chlorobenzoic	222.4	285.3	350.5	398.5	.....	.....
p-Chlorobenzoic	222	285.2	353.5	400	.....	.....
o-Bromobenzoic	223	286.5	352.5	401	.....	.....
m-Bromobenzoic	222.8	285	352.6	401.6	.....	.....
m-Hydroxybenzoic	219.7	285.8	350.8	397.3	.....	.....
m-Acetoxybenzoic	220.4	284	349.1	397	.....	.....
o-Sulphobenzoic	220	284.5	349.5	397.5	.....	.....
m-Sulphobenzoic	220	284.5	349.5	397.5	.....	.....
Picric	207	281.6	331	380	451.6	506.8
Gallic	220	.....	348	396	459.1	514.3
Aminobenzenesulphonic	221	285	350	398	.....	.....
o-Toluic*	.....	.....	.....	397	470.1	536
m-Toluic*	.....	.....	.....	397	470.4	541.9
p-Toluic*	.....	.....	.....	397	469.1	538.8
Mandelic	.....	.....	.....	397	475.4	539.9
Sebacic	218	284	343.5	391	.....	.....

of atoms in the molecule have practically the same μ_∞ value. From these values and the others given in the table just referred to the curve was, therefore, plotted. On this curve it was possible to find the values of μ_∞ for the dibasic acid by means of the graphic method previously described. The curve shows that at the higher temperatures the method is far less accurate, since the values which are determined directly, using the sodium salt, fall less frequently on a definite curve at the higher temperatures.

[1]Carnegie Inst. Wash. Pub. No. 170.

The results of the conductivity measurements are tabulated in the following pages. The molecular conductivities (μ_v) are expressed in Siemens units. Temperature coefficients are expressed in both conductivity units and percentages. The former are obtained by the equation

$$(\mu_{t_1} - \mu_t)/(t_1 - t) = \text{conductivity units};$$

the latter by the equation

$$(\mu_{t_1} - \mu_t)/\mu_t(t_1 - t) = \text{per cent temperature coefficient}^1$$

where t = the lower temperature, t_1 the next higher temperature, μ_t and μ_{t_1} the conductivities of the same solution measured at temperatures t and t_1, respectively.

Obviously the percentage dissociation may be expressed as

$$\alpha = \mu_v/\mu_\infty$$

The dissociation constants are obtained from Ostwald's dilution law

$$\alpha^2/(1-\alpha)V = K$$

This is found to hold for the weaker organic acids. In the tables where no values are given for $K \times 10^4$, the acids were so strong that they did not obey the law.

The following acids were tested, but were found to be either too slightly soluble to work with, or to undergo decomposition:

Nitrocinnamic acid (insoluble).

β-Naphtholdisulphonic acid (insoluble).

Terephthalic acid (insoluble).

Aminosalicylic acid (insoluble).

Aminophenolsulphonic acid (decomposed).

p- and *o*-nitro- and dinitro-phenols were studied, but the conductivities found were so small that the results were not reliable, since the percentage error due to unavoidable experimental errors was relatively large.

In table 18 omitted values have been determined by other investigators, especially those whose values are given at only the higher temperatures.

It has been shown by the work of Ostwald, Jones, and others in this field, that the Ostwald dilution law does not hold for strongly dissociated acids. The "constants" of acids of this class have been omitted. In the tables that were secured in the experimental work, irregular constants are frequently given. These are of value only in determining the relative strengths of such acids.

It had been previously observed that as a rule the percentage dissociations of the organic acids decreased with rise in temperature, but that the values of percentage dissociation of certain acids increased with rise in temperature. In this work, however, it was found that in each case the increase has been at a diminishing rate, and further study showed that the maximum dissociation was reached in all cases except citric acid.

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[1]Zeit. phys. Chem., **2**, 561 (1888).

TABLE 17.—*Conductivities, temperature coefficients, dissociations, and constants.*

Acid.	V	Molecular conductivity.				Temperature coefficients.						Percentage dissociation.				Dissociation constants.			
		0°	12.5°	25°	35°	0° to 12.5°		12.5° to 25°		25° to 35°		0°	12.5°	25°	35°	0°	12.5°	25°	35°
						Con. units.	*P. ct.*	*Con. units.*	*P. ct.*	*Con. units.*	*P. ct.*								
Malic	32	26.84	35.97	44.45	51.18	0.73	2.71	0.67	1.86	0.67	1.50	12.11	12.56	12.62	12.79	5.21	5.63	5.69	5.86
	128	46.73	62.83	78.46	90.47	1.28	2.73	1.25	1.98	1.20	1.52	21.05	21.95	22.28	22.62	4.38	4.82	4.98	5.16
	512	79.42	106.41	132.70	152.89	2.16	2.71	2.10	1.97	2.01	1.51	35.85	37.18	37.69	38.22	3.91	4.29	4.45	4.61
	1024	103.59	138.48	172.50	198.11	2.79	2.69	2.72	1.96	2.56	1.48	46.76	48.38	49.00	49.52	4.03	4.42	4.50	4.74
	2048	128.27	170.97	211.16	243.84	3.41	2.65	3.21	1.87	3.26	1.53	57.90	59.73	59.98	60.96	3.88	4.22	4.38	4.64
Aconitic	32	24.80	33.13	41.29	47.21	0.67	2.68	0.65	1.96	0.59	1.43	11.26	11.61	11.80	11.86	4.46	4.76	4.93	4.98
	128	41.91	55.75	69.28	79.67	1.11	2.63	1.08	1.94	1.01	1.45	19.03	19.54	19.79	19.94	3.49	3.70	3.81	3.87
	512	64.71	85.51	105.67	121.09	1.66	2.56	1.61	1.88	1.54	1.45	29.38	29.98	30.19	30.42	2.38	2.50	2.54	2.59
	1024	79.12	104.19	128.78	146.92	2.00	2.53	1.97	1.88	1.81	1.40	35.93	36.53	36.79	36.91	1.96	2.05	2.09	2.10
	2048	91.19	120.09	149.67	169.80	2.31	2.53	2.37	1.97	2.01	1.34	41.41	42.10	42.76	42.66	1.42	1.49	1.55	1.54
m-Chlorobenzoic	512	52.37	60.79	86.91	98.72	1.39	2.65	1.37	1.96	1.18	1.35	23.55	24.46	24.79	24.52	1.41	1.54	1.59	1.55
	1024	70.06	93.47	115.97	130.39	1.87	2.66	1.80	1.92	1.44	1.24	31.50	32.76	33.08	32.72	1.41	1.55	1.59	1.55
	2048	92.76	120.27	149.13	169.19	2.20	2.37	2.30	1.91	2.00	1.34	41.70	42.15	42.54	42.45	1.45	1.49	1.53	1.52
p-Chlorobenzoic	2048	63.35	85.53	107.61	124.22	1.77	2.79	1.76	2.06	1.66	1.54	28.50	29.90	32.80	31.00	0.554	0.622	0 781	0.680
o-Bromobenzoic	128	95.79	116.50	133.63	144.77	1.66	1.73	1.37	1.17	1.11	0.83	43.40	40.66	37.91	36.04	24.99	21.76	18.08	15.86
	512	142.60	176.40	205.30	226.44	2.70	1.89	2.31	1.30	2.11	1.03	63.94	61.57	58.25	56.46	22.14	19.26	15.87	14.29
	1024	168.96	211.08	247.88	273.87	3.37	1.99	2.94	1.39	2.59	1.04	75.76	73.67	70.34	68.29	23.13	20.12	16.29	14.36
	2048	183.37	233.05	277.56	311.05	3.97	2.16	3.56	1.52	3.35	1.21	82.22	81.34	78.76	77.56	18.56	17.32	14.36	13.08
m-Bromobenzoic	512	50.71	67.80	84.62	97.36	1.36	2.68	1.34	1.97	1.28	1.50	22.76	23.78	23.99	24.24	1.31	1.44	1.47	1.51
	1024	69.42	92.71	115.22	131.78	1.86	2.67	1.80	1.94	1.65	1.43	31.15	32.53	32.67	32.81	1.37	1.53	1.54	1.56
	2048	89.28	121.01	150.72	173.46	2.53	2.83	2.37	1.95	2.27	1.50	40.07	42.45	42.74	43.19	1.31	1.52	1.55	1.60
m-Acetoxybenzoic	128	25.89	34.52	42.71	48.69	0.69	2.66	0.65	1.88	0.59	1.38	11.24	12.15	12.23	12.26	1.11	1.31	1.33	1.38
	512	48.77	64.61	79.78	90.90	1.26	2.58	1.21	1.87	1.11	1.39	22.12	22.75	22.85	22.89	1.22	1.30	1.32	1.32
	1024	65.63	86.72	106.97	122.11	1.68	2.55	1.62	1.86	1.51	1.39	29.77	30.53	30.64	30.75	1.23	1.31	1.32	1.33
	2048	85.45	112.34	138.66	156.64	2.15	2.51	2.10	1.86	1.80	1.29	38.76	39.55	39.71	39.45	1.19	1.26	1.27	1.25

TABLE 17.—*Conductivities, temperature coefficients, dissociations, and constants*—Continued.

Acid.	V	Molecular conductivity.				Temperature coefficients.						Percentage dissociation.				Dissociation constants.			
		0°	12.5°	25°	35°	0° to 12.5°		12.5° to 25°		25° to 35°		0°	12.5°	25°	35°	0°	12.5°	25°	35°
						Con. units.	*P. ct.*	*Con. units.*	*P. ct.*	*Con. units.*	*P. ct.*								
o-Sulphobenzoic	23	226.09	290.63	352.91	401.70	5.16	2.28	4.98	1.71	4.88	1.38	[1]	[1]	[1]	[1]	[1]	[1]	[1]	[1]
	128	236.11	304.14	369.64	421.86	5.44	2.30	5.24	1.72	5.22	1.41	.....	.....	.....	.....	.....	.....	.....	.....
	512	251.85	325.13	394.95	452.16	5.86	2.32	5.58	1.71	5.72	1.44	.....	.....	.....	.....	.....	.....	.....	.....
	1024	256.41	330.96	401.81	452.16	5.96	2.32	5.67	1.71	5.03	1.30	.....	.....	.....	.....	.....	.....	.....	.....
	2048	274.01	356.24	428.67	.....	6.57	2.39	5.79	1.62	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
m-Sulphobenzoic	512	103.67	138.58	174.18	202.11	2.79	2.69	2.84	2.04	2.79	1.60	47.12	48.71	49.83	50.94	[1]	[1]	[1]	[1]
	1024	119.54	159.75	200.06	231.98	3.21	2.68	3.22	2.01	3.19	1.59	54.33	56.15	57.24	58.35	.....	.....	.....	.....
	2048	135.98	181.68	227.20	262.67	3.65	2.68	3.64	1.99	3.54	1.55	61.80	63.85	65.00	66.08	.....	.....	.....	.....
p-Aminobenzenesulphonic	32	61.42	88.45	119.42	146.04	2.16	3.51	2.47	2.79	2.66	2.22	27.79	31.03	34.12	36.69	[1]	[1]	[1]	[1]
	128	77.91	112.51	152.52	187.36	2.76	3.53	3.20	2.84	3.48	2.28	35.25	39.47	43.57	47.07	.....	.....	.....	.....
	512	104.86	149.36	199.06	241.34	3.56	3.39	3.97	3.65	4.22	2.11	47.44	52.40	56.87	60.63	.....	.....	.....	.....
	1024	122.65	169.90	226.13	272.32	3.70	3.01	4.50	2.64	4.61	2.03	55.49	59.61	64.60	68.42	.....	.....	.....	.....
	2048	132.15	182.98	239.16	285.99	4.06	3.07	4.49	2.45	4.68	1.95	59.79	64.20	68.33	71.85	.....	.....	.....	.....
Sebacic	512	[2]	[2]	37.95	42.38	.....	.....	.....	.....	0.44	1.16	.....	.....	11.04	10.83	[1]	[1]	[1]	[1]
	1024	34.27	44.28	53.00	59.43	0.80	2.33	0.69	1.55	0.64	1.20	15.72	15.59	15.43	15.19	.....	.....	.....	.....
	2048	46.42	59.40	71.19	79.60	1.04	2.24	0.94	1.58	0.84	1.17	21.29	20.91	20.72	20.35	.....	.....	.....	.....

[1] Calculations could not be made because of the strength of this acid. [2] Precipitated.

In the work of Springer[1] the maximum dissociation was reached in every case studied by him, except for the amino acids, such as sulphanilic, metanilic, naphthionic, and dinitroaminophenol. Smith did not study acids of this class; but certain groups of those which he has investigated show an increase in dissociation over a wide range in temperature. The acids that show this property to the greatest extent are those containing the hydroxyl (OH) group. These acids have percentage dissociation values which increase, attain a maximum, and then decrease.

TABLE 18.—*Dissociation constants.*

Acid.	0°	12.5°	25°	35°	50°	65°
m-Chlorobenzoic	1.41	1.52	1.57	1.54	....	....
p-Chlorobenzoic	0.55	0.62	0.78	0.68	....	....
o-Bromobenzoic*	....	....	....	....	....	....
m-Bromobenzoic	1.33	1.49	1.52	1.55	....	....
m-Hydroxybenzoic	0.65	0.67	0.68	0.69	....	....
m-Acetoxybenzoic	1.19	1.29	1.41	1.32	....	....
o-Sulphobenzoic*	....	....	....	....	....	....
m-Sulphobenzoic*	....	....	....	....	....	....
Picric*	....	....	....	....	....	....
Gallic	0.36	....	0.38	0.39	0.42	0.40
Aminobenzenesulphonic*	....	....	....	....	....	....
o-Toluic*	....	....	....	1.25	1.00	0.88
m-Toluic*	....	....	....	0.55	0.52	0.46
p-Toluic*	....	....	....	0.44	0.39	0.35
Mandelic*	....	....	....	4.2	3.7	3.5
Sebacic	2.8	2.7	2.6	2.5	....	....
Butyric*	....	....	....	0.140	0.131	0.118
Isobutyric*	....	....	....	0.114	0.121	0.122
Malic	4.28	4.67	4.81	5.00	....	....
Pyrotartaric	0.88	0.85	0.83	....	....	....
Racemic*	....	....	....	....	....	....
Hippuric	2.11	2.20	2.27	2.23	2.32	2.23
Citric*	....	....	....	....	....	....
Aconitic*	....	....	....	....	....	....
Crotonic	0.193	0.206	0.210	0.208	0.023	0.188
Maleic*	....	....	....	....	....	....
Fumaric*	....	....	....	11.3	9.8	8.8
Itaconic*	....	....	....	1.5	1.55	1.54
Citraconic*	....	....	....	35.8	32.9	31.5
Mesaconic*	....	....	....	7.8	7.1	6.4

*Value found by some other investigator; see Publication of the Carnegie Institution of Washington, No. 170.

The temperature coefficients of conductivity expressed in conductivity units, for all of the above acids show an increase with the dilution of the solution and a decrease with rise in temperature. As would be expected, the rate of increase or decrease varies greatly. There seems to be a relation between the strength of the acid and rate of increase or decrease of the temperature coefficients of conductivity with rise in temperature. The stronger the acid the less rapid is the change. It should be noted that strong acids are so largely dissociated at all

[1]Amer. Chem. Journ., 48, 411, (1912).

dilutions that a change in the dilution would change the coefficients very slightly.

The temperature coefficients of conductivity of acids, even of mineral acids to a certain extent, decrease with rise in temperature. The literature shows also that the mineral acids are more or less hydrated in solution. It is evident that an acid which is either unhydrated or only slightly hydrated (as is the case with most of the organic acids studied in this investigation) would show a rapid decrease in the temperature coefficients of conductivity with rise in temperature; since there would be no complex hydrated ion to lose water, and, thus, from this cause, the conductivity could not be increased. This point is illustrated in table 19, which gives the temperature coefficients of certain weak, unhydrated acids at $V = 1024$.

TABLE 19.

Acid.	35°–50°	50°–65°
Butyric.....	0.019	0.013
Isobutyric.....	0.015	0.009
Pyrotartaric....	0.12	0.11

Table 20 from the work of Jones and Wightman,[1] gives similar values for some of the hydrated acids; two weaker acids—racemic and citric—show the same decrease in the coefficients as the strong acids. This indicates that the strength of the acid has very little to do with the gradual decrease in temperature coefficients, but that this decrease is caused by hydration; and the above relation applies to the strong acids only because they are the acids which are the most strongly hydrated. This same

TABLE 20.

Acid.	Water of crystallization H_2O	0°–15°	15°–25°	25°–35°	Percentage decrease.
Meconic.....	3	10.06	9.94	9.18	8.8
Benzenesulphonic.....	1	5.26	5.05	5.06	3.8
p-Toluenesulphonic.....	4	4.92	4.84	4.67	5.3
1, 2, 4-Nitrotoluenesulphonic....	2.5	4.74	4.67	4.35	8.2
Racemic $K_0° = 9.1$.....	1	3.76	3.56	3.43	8.0
Citric $K_0° = 6.85$.....	1	3.64	3.59	3.38	7.1

relation holds in this work. The temperature coefficients of conductivity of the acids are larger for stronger acids. This is shown by table 21, in which the acids are arranged according to their strengths.

All the work done in the Chemical Laboratory of the Johns Hopkins University on the conductivity of organic acids has shown that the temperature coefficients of conductivity expressed in percentage decrease slightly with increasing dilution and more rapidly with rise in temperature. The decrease due to rise in temperature manifests

[1] Amer. Chem. Journ., **46**, 56 (1911).

itself in every case studied, but a large number of exceptions present themselves in the decrease due to increasing dilution. No doubt this is the result of hydrolysis.

TABLE 21.

[Temperature coefficients, 35°–50°; $V = 1024$.]

Acid.	Cond. units.	K
Isobutyric	0.316	0.114
Crotonic	0.54	0.208
Itaconic	1.62	1.55
Mandelic	1.83	4.2
o-Sulphobenzoic	5.12	100 per cent diss.

In all the acids that Smith studied, the percentage temperature coefficients of conductivity are small and are of the same order of magnitude. The decrease is regular as the temperature rises. This indicates that some constant factor has influenced the solution,[1] such as the viscosity of the medium.

The isomeric acids have been the subject of a large amount of investigation. Ostwald,[2] Walker,[3] and Derrick[4] have worked on the correlation of ionization and structure for such acids, and on the effect of substitution. This work has confirmed the following statement of Springer and Jones:

"In the case of isomeric acids containing two carboxyl groups, the acid with these groups in the 'ortho' or the 'cis' position is always the stronger."

o-Toluic 35°,	$K = 1.25$	Maleic (cis) 35°,	$K = 154$
m-Toluic 35°,	$K = 0.55$	Fumaric (trans) 35°,	$K = 11.3$
p-Toluic 35°,	$K = 0.44$	Citraconic (cis) 35°,	$K = 35.8$
m-Bromobenzoic 35°,	$K = 1.55$	Mesaconic (trans) 35°,	$K = 7.8$

o-Bromobenzoic 35°, too strong to give a constant.

Euler[5] showed that the conductivity of organic acids is a parabolic function of the temperature. This was also brought out by the work of White and Jones. Wightman and Jones, and Springer and Jones plotted curves, using conductivities as ordinates and temperatures as abscissas, and calculated the conductivity of a number of acids from Euler's formula:

$$\mu_t = \mu_0 + at - bt^2$$

This was always found to hold. It holds also in this work.

The dissociation of a large number of organic acids decreases with rise in temperature. As mentioned above, in certain cases the percentage dissociation apparently attains a maximum at one of the intermediate temperatures, usually at 25° or 35°. This has been observed and noted in the publications of Euler,[6] Schaller,[7] White and Jones,[8]

[1] Jones and West; Amer. Chem. Journ., **34**, 418 (1905).
[2] Zeit. phys. Chem., **3**, 170 (1889).
[3] Journ. Chem. Soc., **61**, 605 (1892); **67** 147 (1895).
[4] Journ. Amer. Chem. Soc., **33**, 1881 (1911); **34**, 74 (1912).
[5] Zeit. phys. Chem., **21**, 257 (1896).
[6] *Ibid.*, **21**, 247 (1896).
[7] *Ibid.*, **25**, 497 (1898).
[8] Amer. Chem. Journ., **44**, 196 (1910).

and Wightman and Jones,[1] but thus far no one has offered a satisfactory explanation. The problem is not simple, there being many factors, any one of which might greatly influence the dissociation. As is well known, decrease in the association of the solvent and in its dielectric constant would greatly affect the conductivity. The effect of rise in temperature has been shown to diminish both the association and the dielectric constant of the solvent. The nature of the dissolved substance itself plays, of course, no small role in the effect on the conductivity of its solution.

Table 22 shows agreement in results in the cases of a few acids studied. The examples were chosen at random and are typical.

TABLE 22.

Acid.	V.	White and Jones.	Smith and Jones.	Ostwald.
Maleic, 35°	32	198.8	197.6	.....
	1024	384.6	384.97	.....
	2048	400.8	400.10	.....
Gallic, 35°	64	19.36	19.46	.....
	1024	71.18	71.20	.....
	2048	96.7	96.82	.....
Hippuric, 25°	128	.....	55.16	54.3
	1024	.....	133.96	131.1
m-Hydroxybenzoic, 25°	32	.....	18.38	18.18
	512	.....	68.24	67.90
	1024	.....	93.15	91.63
Gallic, 25°	64	16.90	16.92	16.83
	512	48.33	48.31	47.74
	1024	62.50	62.56	66.53
	2048	85.02	85.10	.....
Malic, 25°	128	.....	78.46	71.52
	512	.....	132.70	128.1
	1024	.....	172.50	166.6
	2048	.....	211.16	213.0

SUMMARY.

Most of the relations previously established by Jones and his coworkers have been confirmed in this investigation. The mere statement of some of these relations is sufficient, since a glance at the data alone will show that they hold.

1. The temperature coefficients of conductivity increase rapidly with dilution, and decrease rapidly with rise in temperature for the weak organic acids. However, if the acids are hydrated the temperature coefficients of conductivity are larger, and the rate of increase or decrease just mentioned is much slower. The stronger the organic acid the larger these units.

2. The percentage temperature coefficients of conductivity are small, are of the same order of magnitude, and decrease with rise in temperature.

[1] Amer. Chem. Journ., **46**, 56 (1911).

3. The conductivity of most organic acids is a parabolic function of the temperature, as has been pointed out by Euler. His formula

$$\mu_t = \mu_0 + at - bt^2$$

has been shown to hold in every case.

4. The relative strength of organic acids is not dependent upon the temperature.

5. "There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between 25° and 35°, while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from 0°."

6. Isomeric acids do not behave similarly with regard to change in their dissociation.

7. Strong organic acids, as is well known, do not obey the Ostwald dilution law.

8. The "ortho" and "cis" forms of isomeric acids are the stronger, i. e., have the larger constants.

9. The migration velocities of the anions are functions of the number of atoms that are present in them. As has already been pointed out in this paper, this fact was made use of in determining the μ_∞ values of dibasic acids.

10. Most dibasic acids dissociate like monobasic acids.

11. "The behavior of the organic acids with respect to the change in their dissociation with the temperature, is not in accord with the hypothesis of Thomson-Nernst, which connects dissociating power and dielectric constants; or at least the influence of some other unknown factor is suggested."

CHAPTER III.

A PRELIMINARY STUDY OF THE CONDUCTIVITY OF CERTAIN ORGANIC ACIDS IN ETHYL ALCOHOL AT 15°, 25°, AND 35°.

By E. P. Wightman and J. B. Wiesel.

Considerable work has been done, in the Chemical Laboratory of the Johns Hopkins University, especially within the last five years, on the conductivity and dissociation of organic acids in water as a solvent, over a fairly wide range of temperature and dilution; and a number of interesting relationships have been pointed out.[1] Since, up to the present, almost nothing has been done with these acids in absolute alcohol, we decided to extend our investigations on the organic acids into this field.

HISTORICAL.

A few rather crude measurements of the conductivity of hydrochloric acid and some inorganic salts had been made in alcohol-water mixtures as early as 1882. The first work which need be mentioned is that of Kablukoff[2] in 1889. He determined the conductivity of hydrochloric acid in alcohol and some other solvents, and in mixtures of alcohol and water, and showed that molecular conductivity increased markedly with decrease in amount of alcohol and increased slowly with the dilution.

Wakeman,[3] in 1893, measured the conductivities of some organic acids, as well as of hydrochloric acid, potassium chloride, and sodium chloride, in mixtures of alcohol and water ranging from pure water to 50 per cent alcohol. Using Lentz's[4] values for the relative migration velocities of hydrogen, sodium, and potassium in water and mixtures of water and alcohol, and employing the method of Ostwald[5] for determining the μ_∞ values for the organic acids from their sodium salts, he calculated the dissociations of these acids. He also calculated dissociation constants by means of Ostwald's dilution law. His dissociation values decrease slowly with increase in alcohol. The constants decrease much more rapidly for the same increase in alcohol. Wakeman plotted curves (fig. 21) with molecular conductivities as ordinates and percentage alcohol as abscissæ, and showed that when they were extended beyond 50 per cent alcohol in the direction of 100 per cent alcohol, the conductivity probably approached zero as a limit. He concluded that dissociation in the mixtures is much less than would

[1]Publication 170, Part II, Carnegie Inst. Wash.; see also Amer. Chem. Journ., **44**, 156 (1910); **46**, 56 (1911); **48**, 320, 411 (1912); **50**, 1 (1913).
[2]Zeit. phys. Chem., **4**, 429 (1889).
[3]*Ibid.*, **11**, 49 (1893).
[4]Mem. de l'Acad. de St. Petersb., VII series, vol. **30**, 9 (1882).
[5]Zeit. phys. Chem., **2**, 270 (1888); *ibid.*, **3**, 170 (1889); see also, Amer. Chem. Journ., **46**, 66 (1911).

be expected, and that the Ostwald dilution law could not be applied to the mixtures containing much alcohol.

In 1894 Schall[1] determined the conductivity of oxalic, dichloracetic, picric, and hydrochloric acids in methyl alcohol, in ethyl alcohol, in ethyl alcohol-water mixtures, and in isobutyl alcohol. He concluded from his results that molecular conductivity is much less in the alcohols than in water, and that the acids behave very differently in alcohol-water mixtures than in the pure solvents; some acting just the opposite from what might be expected from their behavior in the pure solvents. For instance, picric acid gives a much higher, and the others much lower, conductivity values in water-alcohol mixtures than in the pure alcohol.

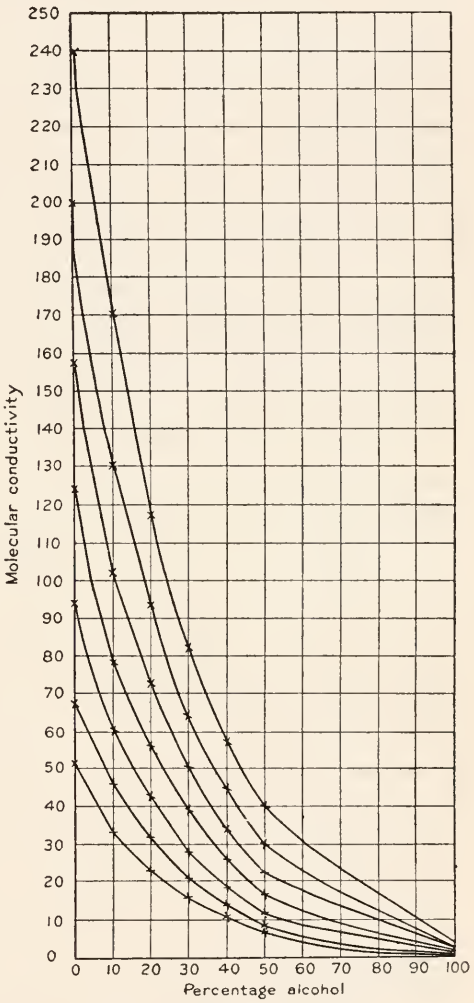

FIG. 21.—Monobromacetic acid.

A careful piece of work on the conductivity of certain organic acids, acetic, monochloracetic, dichloracetic, trichloracetic, and succinic acids, and of hydrochloric acid in absolute alcohol at 18° was carried out, in 1894, by Wildermann.[2] The alcohol was freed from aldehyde by treatment with silver nitrate, and from water by heating with calcium oxide. Great care was exercised in protecting the alcohol from the air, and a special apparatus was constructed for drawing a measured quantity of alcohol out of the supply bottle directly into the conductivity cell, which had a capacity of about 25 c.c. In order to make his minimum points on the bridge more distinct, Wildermann employed a graphite resistance rheostat which he constructed and standardized against a known resistance. He states that his conductivity cells had to be washed with running water for about 8 to 10

[1]Zeit. phys. Chem., **14**, 701 (1894). [2]*Ibid.*, **14**, 231 (1894).

days. On washing with alcohol and drying, it was found that the alcohol which was in contact with the platinum electrodes was oxidized by the air, even when this was thoroughly purified and dried, to acetic acid, which, of course, increased the conductivity of the alcohol. Therefore, instead of drying after washing with water and draining, alcohol was introduced so as first to wash the glass walls, and then the alcohol was allowed to cover the electrodes. Some of this alcohol was then drawn off by means of a pipette and fresh alcohol was introduced, keeping the electrodes continuously covered, until all the water had been eliminated and the conductivity values after each removal and addition of fresh alcohol remained unchanged. Says Wildermann, "this cost a half day of work and 300 to 500 c.c. of good absolute alcohol." The same procedure was adopted for dilute solutions of the acids, the strength of any solution being determined by titration. He does not give any tables of his results with the weaker acids—acetic, monochloracetic, and succinic. He simply makes the qualitative statement that these substances between volumes 10 and 160 give a molecular conductivity which increases approximately proportional to the square root of the volumes; that is $\frac{\mu_{v_1}}{\mu_v}$ is about equal to $\sqrt{\frac{v_1}{v}}$, v being the greater of the two volumes.

Wildermann draws the following conclusions:

"(1) Under about 10 liters for dichloracetic acid, the values of $\frac{\mu_{v_1}}{\mu_v}$ are less than those of $\sqrt{\frac{v_1}{v}}$; above about 10 liters the value of $\frac{\mu_{v_1}}{\mu_v}$ is greater than $\sqrt{\frac{v_1}{v}}$; in dilutions from 800 to 2,000 liters the values of $\frac{\mu_{v_1}}{\mu_v}$ become almost equal to $\frac{v_1}{v}$. The increase of $\frac{\mu_{v_1}}{\mu_v}$ is therefore continuous, not only in the concentrated solutions, but also in the more dilute solutions to which the equation $\frac{\mu_\infty(\mu_\infty - \mu_v)}{\mu_v^2} v = k$ may be applied."

"(2) The same conclusions are even more nearly true in the case of β-resorcylic acid."

(3) In the case of trichloracetic acid there is, just as above, an increase in $\frac{\mu_{v_1}}{\mu_v}$ from 20 to 300 liters, above which the $\frac{\mu_{v_1}}{\mu_v}$ value becomes almost equal to $\sqrt{\frac{v_1}{v}}$ and then increases throughout the more dilute solutions.

That this is true, even at a different temperature from 18°, is shown in some later work by the author, using an entirely independent method. An explanation, however, had already been offered for the phenomenon

in a previous paper by the author.[1] In this earlier work he was studying the effect of the presence of the large amount of the undissociated portion of weakly dissociated acids, upon the conductivity and dissociation values and upon the dissociation constants. It had been pointed out by Ostwald that in aqueous solutions the degree of dissociation, for the same dilutions of trichloracetic, dichloracetic, monochloracetic, and acetic acids shows a decrease in passing from the trichlor derivative to the acetic acid in the order named. A like succession was observed by Wildermann for the same acids in alcohol.

(4) For hydrochloric acid in alcohol, results analogous to those in water were obtained. A maximum value of the conductivity was noted.

In summing up, Wildermann says that it is possible to apply the Kohlrausch method to the determination of the conductivity of strong organic or inorganic acids in absolute alcohol, but that no reliable results could be obtained for such weak acids as acetic, monochloracetic, and succinic. He remarks that much time and patience on the part of the experimenter are required to obtain results that are at all reliable.

In a second investigation by Wildermann[2] the same acids as in the earlier work were studied, using in this case a precision galvanometer method and working at 25° instead of at 18°. He arrived at precisely the same conclusions as before, except that he found the precision method susceptible of more general application than that of Kohlrausch.

Among those who have worked on conductivity in alcohol since Wildermann are, Zelinsky and Krapiwin,[3] who determined the conductivity of a number of inorganic salts and acid salts of organic acids; Ernest Cohen,[4] who obtained the conductivity and dissociation of several inorganic salts in absolute methyl alcohol at 18°, and who states that because of the action of the platinum electrodes upon the solutions, measurements were unsafe at higher temperatures; Roth,[5] whose work had to do with the conductivity of potassium chloride in alcohol-water mixtures; and others of minor importance.

Some still more recent work[6] has been done in this laboratory with inorganic salts both in methyl and in ethyl alcohol and alcohol-water mixtures, but it need not be discussed here. (See Chapter IV.)

EXPERIMENTAL.

The conductivity apparatus used for making the measurements was similar to that employed in previous work in this laboratory, except that on account of the high resistances offered by the alcoholic solutions of the acids, it was necessary to make use entirely of the cylindrical type of conductivity-cell. The method of obtaining their constants has previously been described[7] and need not be dealt with here.

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[1] Ber. d. chem. Gesell., **26**, 1782–1783 (1893).
[2] Zeit. phys. Chem., **14**, 247 (1894).
[3] *Ibid.*, **21**, 35 (1896).
[4] *Ibid.*, **25**, 1 (1898).
[5] *Ibid.*, **42**, 209 (1903).
[6] Carnegie Inst. Wash. Pubs. Nos. 80 and 180.
[7] Amer. Chem. Journ., **42**, 527 (1909); **44**, 64 (1911).

Since the percentage temperature coefficients of conductivity for substances in alcohol, as well as the coefficient of expansion of the alcohol itself, are so large, it is necessary to have fairly close temperature regulation. This was secured by the combination of a specially devised gas regulator and thermo-regulator. These have already been described[1] in earlier papers.

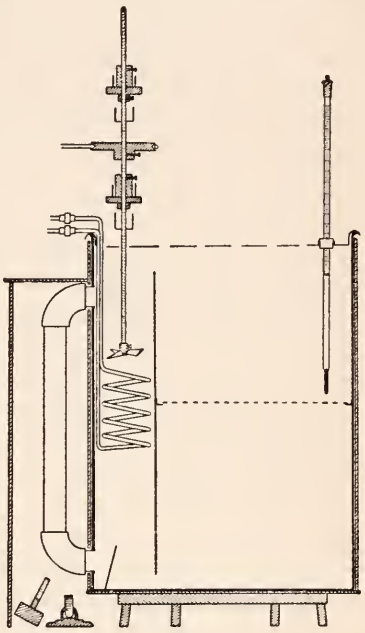


FIG. 22.

In cooperation with Dr. P. B. Davis, of the Chemical Laboratory of the Johns Hopkins University, a new form of constant-temperature bath was also designed. Its construction can be seen from fig. 22. A full discussion of the form finally adopted will be presented in a paper soon to be published by Jones, Davis, and Putnam.[2] In these baths the temperature ordinarily does not vary more than 0.02° C., which is sufficiently constant for our purpose. With special precautions as to insulation from changes in temperatures, and a further modified form of the thermo-regulator, the variation can be decreased to a few thousandths of a degree. Aside from the better temperature regulation obtained in this new form of thermostat-bath, there are also one or two other advantages derived from its use. The apparatus is of copper which does not rust, and the stirring arrangements and the cooling coil are on the side, and are therefore out of the way. A number of minor improvements were likewise added.

Solutions were made up in 200 c.c. flasks calibrated for 25°, and the conductivity measurements of these solutions were taken at 15°, 25°, and 35°. Pipettes were frequently used for measuring purposes because of greater ease in handling. They were carefully calibrated. Corrections for the expansion and contraction of the alcoholic solutions at 35° and 15°, respectively, were of course applied to the conductivity measurements.

The alcohol was prepared by heating ordinary 95 per cent alcohol for several days with fresh, unslaked lime in a copper tank, provided with a ground-brass stopper and reflux condenser, and then distilling through a block-tin condenser. The distillate thus prepared was reheated with fresh lime and again distilled, the first and last portions

[1]Zeit. phys. Chem., **85**, 519 (1913); Journ. Chim. Phys. July 1914.
[2]See Chapter VI of this monograph.

of this distillate being discarded. A few sticks of sodium hydroxide added during the last day of heating insured the removal from the distillate of any aldehyde which might have been present, and which otherwise would have distilled over with the alcohol. It is possible, by taking proper precautions in the manner of handling, to obtain by such a method alcohol having a specific gravity of 0.78506, to within the limits of experimental error, +0.00002. According to Circular 19 of the Bureau of Standards, alcohol with this specific gravity has no water in it; that is, it is 100 per cent alcohol. The alcohol employed in the conductivity measurements varied in specific gravity from the value of 0.78506 to 0.78517, the latter containing 99.964 per cent alcohol. The receiver for the distillate was a 6-liter Jena glass bottle. The stopper was a three-holed paraffined cork. Through one hole passed a siphon, through another an adapter with a glass stopcock, and through the third a calcium chloride-soda lime tube also having a glass stopcock. In this way the alcohol was well protected during distillation from impurities in the air, and small quantities sufficient for making up the solutions could be drawn off without exposing the main supply. After weighing out the quantity of dried and purified acid necessary to make a solution of the required normality, the acid was washed off the watch glass or out of the weighing bottle into a funnel, and then into a 200 c.c. Jena flask which had previously been thoroughy washed with water, and then with some of the alcohol with which the solution was to be made up. The flask was filled to the neck with alcohol and shaken until all the acid had dissolved. It was finally hung in a 25° thermostat-bath until temperature equilibrium was reached, and then filled to the mark. In the meantime a conductivity-cell which had been thoroughly washed the day before and in which pure alcohol had been allowed to stand over night, was dried with filtered dry air. It was then rinsed several times with portions of the solution which had just been made up, and finally nearly filled with this solution introduced as shown in figure 23. A little carbonate is formed by opening in this way to the air, but it is a very small quantity, and in the course of a few days is entirely precipitated to the bottom of the bottle. T and T' are filled with a mixture of calcium chloride and soda-lime to protect the alcoholic solution when the stopcocks S and S are opened. The stoppers in T and T' are of cork and are thoroughly paraffined. A system such as this remains protected from the air for a period of several months.

The alcoholic solution, in course of time, becomes colored slightly yellow, but its alkaline concentration is apparently not changed, as can be seen by comparing titrations made against a standard acid in February and again in May:

On Feb. 25, 10 c.c. of standard acid = 8.87 c.c. of alkali.
On May 7, 10 c.c. of standard acid = 8.87 c.c. of alkali.

The bottle containing the alkali was covered with a dark material, since, in the presence of light the tendency of the alkaline solution to become colored is much greater than in the dark.

One of the greatest difficulties in connection with the alcoholic potash method was that of temperature changes. The coefficient of expansion of alcohol is so large that even small changes in the temperature of the laboratory, and consequent changes in temperature of the solution, will change quite appreciably the normality of the alkali.

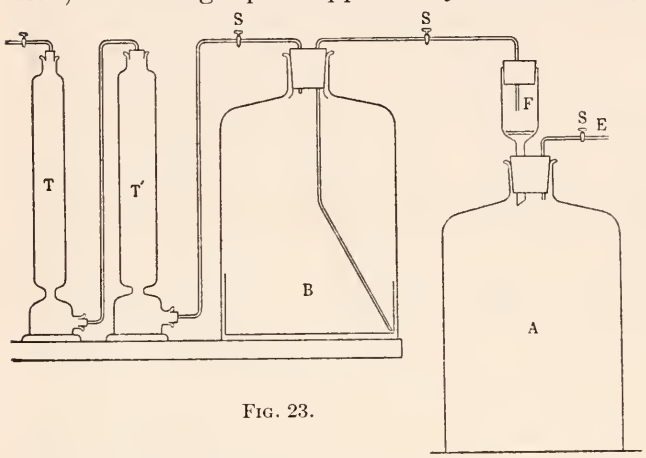


FIG. 23.

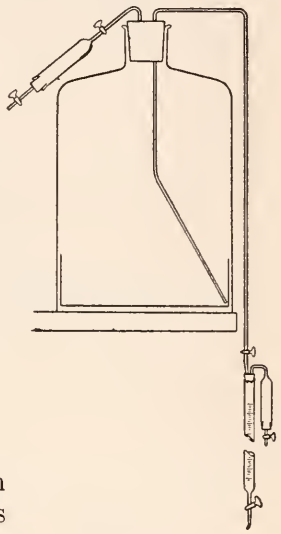


FIG. 24.

It was this difficulty which led us to the use of an aqueous solution of ammonia with coralline as the indicator, instead of the alcoholic caustic potash with phenolphthalein as the indicator. The ammonia was prepared by heating concentrated ammonia and passing the gas which was given off, first over sticks of sodium hydroxide, which collected a large part of the water-vapor and any carbon dioxide, and then over sodium, which absorbed the remainder of the water-vapor; and finally into a weighed quantity of conductivity water in a measuring flask until the approximate amount of the gas necessary to make a tenth-normal solution was dissolved. This solution was titrated against standard sulphuric acid to obtain its exact normality.

Coralline was used as the indicator because it is sensitive to the organic acids, and is not sensitive to carbon dioxide except when the latter is present in fairly large quantity. In order to test whether coralline is sensitive to small quantities of carbon dioxide, another worker in this laboratory measured out two equal quantities of a standard acid, added an equal amount of coralline to each, and then allowed carbon dioxide to bubble through one of these solutions for some minutes. Titrations of both solutions were made, and practically no effect due to the presence of carbon dioxide was found. Equal volumes of a standard acid were again titrated, this time after having

passed carbon dioxide into one of the solutions for a considerable time. There was a small difference in the titration values. In both cases the amount of carbon dioxide passed into the solutions was infinitely more than would ordinarily be present in such solution as we were titrating.

It was at first thought advisable to use an alcoholic solution of potassium hydroxide for titration purposes. There are, however, several difficulties involved. An approximately tenth-normal solution of potassium hydroxide in absolute alcohol was made up and allowed to stand for a couple of days. The carbonate settled, leaving a clear supernatant solution. But if the bottle was opened even for a very short time the solution became cloudy, and when poured into a burette became white with precipitated carbonate.

A method of filtering the solution, being a modification of one previously used in this laboratory, was then adopted, together with an arrangement for siphoning the solution out of the bottle into the burette. Figure 23 shows the design of the filtering apparatus. The tower T contains sticks of sodium hydroxide and T' is partly filled with metallic sodium. The former acts as a protecting agent to the latter, which serves both for removing the last traces of carbon dioxide and for drying the air. B is a clean empty bottle which is later interchanged with a bottle filled with an alcoholic solution of potassium hydroxide prepared from freshly distilled alcohol. The tube E is connected with suction, so that dried, purified air passes through the whole system, including the Gooch funnel F, containing asbestos previously washed with an alcoholic solution of potassium hydroxide and then pure alcohol, and through the receiving bottle A. When the system has been thoroughly cleansed with dry air free from carbon dioxide, the stopcocks S are closed, and the bottle B is replaced by the one containing alcoholic potash. The stopcocks are then opened and suction again applied to E. When all the solution has been filtered, A is removed, and, as quickly as possible, the stopper arranged to connect it by a siphon with the burette (fig. 24). It was found necessary to use 8 to 10 drops of the solution of coralline in alcohol for each titration. Even then the end-point is not quite as sharp and distinct as with phenolphthalein.

When calculating the concentration of the organic acid in the alcohol from the values obtained by titrating against ammonia, it was found that a slightly different value for the concentration was obtained from that found from the titrations against alcoholic caustic potash. We decided, if possible, to find the cause of this and to apply any necessary corrections. A known quantity of the standard sulphuric acid was titrated against alcoholic potassium hydroxide, using phenolphthalein as the indicator. Several titrations were made in every case, and then an equal quantity of the acid was titrated against the base, using coralline.

The results in the latter case did not agree with those in the former by about 0.2 c.c., 10 c.c. of acid being employed in each case. That the difference was not due to carbon dioxide which might have been dissolved in the sulphuric acid, can be seen from the fact that the same difference appeared in the titrations with an organic acid dissolved in absolute alcohol in which carbon dioxide is not very soluble.

It was found that if the same quantity of phenolphthalein or coralline used when making the ordinary titrations was added either to pure alcohol or to water, and if these solutions of the indicators alone were titrated against the alkali and then back against the standard acid, an appreciable quantity of alkali was required to change the color in one direction, and about as much of the standard acid to change it in the reverse direction, the alkali and acid being of very nearly the same strength. Corrections for the amounts of alkali and acid necessary to produce such color changes were then applied to the titration volumes of the sulphuric acid and alcoholic potash, when agreement to within the limits of experimental error was obtained between the results for the two indicators.

In all the titrations in which alcoholic potassium hydroxide was used its temperature was recorded, and when different from 25°, which was chosen as the standard temperature, a volume correction was applied. It was easy, and was found necessary as well, to keep all the other solutions, particularly those of the organic acids in alcohol, as well as the alcoholic potash, at the standard temperature.

The titration values of the ammonia and standard acid were also corrected, as just stated, for the amounts necessary to produce color change, and the concentration of the ammonia was then calculated. The normality of 1–2–4 dinitrobenzoic acid in alcohol was determined from this standardized ammonia, making the same corrections as above; and it agreed to within 0.2 per cent with that obtained by means of potassium hydroxide. Similar corrections were, therefore, applied to the titrations of all the organic acids.

The sulphuric acid used to standardize the alkali was made up in large quantity, and its normality determined by the usual barium-sulphate method.

Owing to the large amount of preliminary work required, it has been possible up to the present to make conductivity measurements of only 9 organic acids. The same methods of purifying the acids were employed as when the conductivities of these acids were determined in aqueous solution. In most cases the various dilutions were made up by directly weighing the acid.

In the work in alcohol it was necessary to discard all of the weaker organic acids; this, in spite of the fact that our cell constants were about eight times smaller than those of Wildermann. After trying acetic acid several times, we gave up hope of obtaining satisfactory results

with such weak acids. Even the strongest acids with which we worked do not give a molecular conductivity greater than unity.

Titrations of the acids against the standard alkali were made simultaneously with the conductivity measurements at every temperature. At first the alcoholic solution of the acid was not kept at a constant temperature, but it was soon found that in order to obtain comparable results, and to avoid the considerable fluctuations of laboratory temperature, it was necessary to have all the solutions continuously at one temperature, preferably at 25°.

RESULTS.

In the following tables of conductivity, V_m signifies the volume for which the solutions were made up; V_c is the corrected volume. The corrections applied were both for expansion or contraction of the alcohol, and for change in the concentration of the acid due to formation of ester. Molecular conductivity was calculated in the usual manner. Temperature coefficients and percentage temperature coefficients are expressed for 10 degrees. The specific conductivities of the alcohol as given are all multiplied by 10^3. They are really of the magnitude 10^{-7}.

TABLE 23.—*Molecular conductivities, temperature coefficients, etc., of certain acids.*

Malonic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
8	8.12	0.0190	Apr. 16, 1h 00m p.m.
32	32.9	0.0434	16, 1 05 p.m.
128	129.3	0.0775	17, 12 20 p.m.
512	512.8	0.2533	17, 12 45 p.m.
Alcohol	Sp. cond.	0.000254	16, 1 10 p.m.
Alcohol	Sp. cond.	0.000246	17, 12 45 p.m.
		25°	
8	8.13	0.0237	16, 2 35 p.m.
32	33.20	0.0555	16, 2 40 p.m.
128	129.5	0.0985	17, 2 40 p.m.
512	514.9	0.3160	17, 2 45 p.m.
Alcohol	Sp. cond.	0.000257	16, 2 45 p.m.
Alcohol	Sp. cond.	0.000249	17, 2 50 p.m.
		35°	
8	8.18	0.0319	16, 4 30 p.m.
32	33.7	0.0737	16, 4 35 p.m.
128	129.6	0.1351	17, 4 20 p.m.
512	518.1	0.4338	17, 4 25 p.m.
Alcohol	Sp. cond.	0.000258	16, 4 40 p.m.
Alcohol	Sp. cond.	0.000246	17, 4 30 p.m.

Temperature coefficients.

V_m	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct.*
8	0.0046	24.5	0.0075	32.2
32	0.0113	26.7	0.0165	30.7
128	0.0207	26.9	0.0360	37.0
512	0.0613	24.2	0.1145	36.4

o-Chlorobenzoic acid.

V_m	V_n	μ_v	Time of reading.
		15°	
8	8.14	0.01303	Mar. 18, 10h 40m p.m.
32	33.1	0.01530	18, 10 45 p.m.
128	129.5	0.0279	19, 10 50 p.m.
512	513.8	0.1330	19, 11 15 p.m.
Alcohol	Sp. cond.	0.000531	18, 11 20 p.m.
Alcohol	Sp. cond.	0.000540	19, 11 30 p.m.
		25°	
8	8.16	0.0159	18, 11 20 a.m.
32	33.60	0.0198	18, 11 45 a.m.
128	129.7	0.0371	19, 12 35 p.m.
512	516.5	0.1714	19, 12 40 p.m.
Alcohol	Sp. cond.	0.000578	18, 11 50 a.m.
Alcohol	Sp. cond.	0.000622	19, 12 45 p.m.
		35°	
8	8.28	0.0197	18, 4 45 p.m.
32	34.9	0.0271	18, 4 50 p.m.
128	129.8	0.0555	19, 4 55 p.m.
512	519.9	0.2497	19, 5 00 p.m.
Alcohol	Sp. cond.	0.000637	18, 5 00 p.m.
Alcohol	Sp. cond.	0.000711	19, 5 10 p.m.

Temperature coefficients.

V_m	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct.*
8	0.00281	21.1	0.0040	25.9
32	0.00407	27.5	0.0060	31.2
128	0.00903	32.8	0.0181	49.2
512	0.0374	28.1	0.0759	44.6

TABLE 23.—*Molecular conductivities, temperature coefficients, etc., of certain acids*—Continued.

p-Chlorobenzoic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
8	10.0	0.0017	Mar. 26, 12h 30m p.m.
32	33.69	0.0082	26, 12 35 p.m.
128	129.7	0.0157	Apr. 1, 12 30 p.m.
512	514.8	0.1263	1, 12 35 p.m.
Alcohol	Sp. cond.	0.000585	Mar. 26, 12 40 p.m.
Alcohol	Sp. cond.	0.000586	Apr. 1, 12 45 p.m.
		25°	
8	10.08	0.0025	Mar. 26, 2 50 p.m.
32	34.18	0.0117	26, 2 55 p.m.
128	130.3	0.0189	Apr. 1, 3 10 p.m.
512	520.0	0.1547	1, 3 15 p.m.
Alcohol	Sp. cond.	0.000650	Mar. 26, 3 00 p.m.
Alcohol	Sp. cond.	0.000656	Apr. 1, 3 20 p.m.
		35°	
8	10.11	0.0035	Mar. 26, 4 40 p.m.
32	34.9	0.0160	26, 4 45 p.m.
128	130.9	0.0270	Apr. 3, 4 10 p.m.
512	522.7	0.1853	3, 4 15 p.m.
Alcohol	Sp. cond.	0.000753	Mar. 26, 4 50 p.m.
Alcohol	Sp. cond.	0.000827	Apr. 3, 4 20 p.m.

Temperature coefficients.

V_m	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct.*
8	0.00052	42.2	0.00079	39.8
32	0.00315	40.2	0.00382	34.7
128	0.00314	19.9	0.0079	42.4
512	0.0268	27.2	0.0293	19.2

p-Bromobenzoic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
8	8.147	0.00264	Apr. 28, 11h 40m a.m.
32	32.57	0.01252	28, 11 45 a.m.
128	129.1	0.0349	29, 11 10 a.m.
512	512.8	0.1651	29, 11 15 a.m.
Alcohol	Sp. cond.	0.000217	28, 11 50 a.m.
Alcohol	Sp. cond.	0.000214	29, 11 20 a.m.
		25°	
8	8.24	0.00353	28, 2 00 p.m.
32	33.3	0.0147	28, 2 10 p.m.
128	129.2	0.0418	29, 12 25 p.m.
512	517.5	0.1976	29, 12 30 p.m.
Alcohol	Sp. cond.	0.000216	28, 2 20 p.m.
Alcohol	Sp. cond.	0.000262	29, 12 35 p.m.
		35°	
8	8.27	0.0047	28, 4 45 p.m.
32	34.33	0.0200	29, 4 50 p.m.
128	129.5	0.0559	28, 4 00 p.m.
512	518.9	0.2637	29, 4 05 p.m.
Alcohol	Sp. cond.	0.000264	28, 4 55 p.m.
Alcohol	Sp. cond.	0.000233	29, 4 15 p.m.

Temperature coefficients.

V_m	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct.*
8	0.0008	30.7	0.0012	34.9
32	0.0019	15.4	0.0046	32.3
128	0.0068	19.6	0.0138	33.3
512	0.0307	18.6	0.0607	29.9

o-Nitrobenzoic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
8	8.21	0.00785	Apr. 23, 12h 35m p.m.
32	33.19	0.0204	23, 12 40 p.m.
128	129.3	0.0460	27, 12 30 p.m.
512	512.5	0.1788	27, 12 25 p.m.
Alcohol	Sp. cond.	0.000232	23 12 50 p.m.
Alcohol	Sp. cond.	0.000227	27 12 35 p.m.
		25°	
8	8.27	0.00937	23, 2 20 p.m.
32	34.30	0.0253	23, 2 40 p.m.
128	129.5	0.0477	27, 2 40 p.m.
512	517.0	0.2452	27, 2 50 p.m.
Alcohol	Sp. cond.	0.000242	23, 2 50 p.m.
Alcohol	Sp. cond.	0.000238	27, 2 50 p.m.
		35°	
8	8.27	0.0120	23, 4 30 p.m.
32	34.95	0.0337	23, 4 35 p.m.
128	129.6	0.0734	27, 4 30 p.m.
512	518.5	0.2877	27, 4 35 p.m.
Alcohol	Sp. cond.	0.000237	23, 4 45 p.m.
Alcohol	Sp. cond.	0.000232	27, 4 40 p.m.

Temperature coefficients.

V_m	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct.*
8	0.00142	18.56	0.0025	27.45
32	0.0040	20.31	0.0073	30.90
512	0.0642	35.94	0.0413	17.00

p-Nitrobenzoic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
32	32.96	0.0102	Apr. 21, 12h 05m p.m.
128	129.2	0.0516	21, 12 10 p.m.
512	512.8	0.1417	22, 12 05 p.m.
Alcohol	Sp. cond.	0.000237	21, 12 15 p.m.
Alcohol	Sp. cond.	0.000236	22, 12 15 p.m.
Alcohol	Sp. cond.	0.000231	22, 12 20 p.m.
		25°	
32	33.61	0.0151	21, 2 45 p.m.
128	129.3	0.0570	21, 2 50 p.m.
512	517.6	0.1814	22, 2 35 p.m.
Alcohol	Sp. cond.	0.000237	21, 2 50 p.m.
Alcohol	Sp. cond.	0.000227	22, 2 45 p.m.
Alcohol	Sp. cond.	0.000227	22, 2 50 p.m.
		35°	
32	34.56	0.0214	21, 4 50 p.m.
128	129.5	0.0785	21, 4 55 p.m.
512	520.5	0.2399	22, 4 35 p.m.
Alcohol	Sp. cond.	0.000232	21, 4 00 p.m.
Alcohol	Sp. cond.	0.000219	22, 4 40 p.m.
Alcohol	Sp. cond.	0.000216	22, 4 45 p.m.

Temperature coefficients.

V_m	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct.*
32	0.0045	45.5	0.0055	38.2
128	0.0053	10.3	0.0212	37.5
512	0.0380	26.8	0.0565	31.4

TABLE 23.—*Molecular conductivities, temperature coefficients, etc., of certain acids*—Continued.

1, 2, 4 Dinitrobenzoic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
8	8.13	0.0379	Feb. 27, 12h 00m m.
32	33.62	0.0964	Mar. 3, 12h 10m p.m.
128	133.50	0.2556	Feb. 27, 12 25 p.m.
Alcohol	Sp. cond.	0.000882	27, 12 25 p.m.
Alcohol	Sp. cond.	0.000936	Mar. 3, 10 35 a.m.
		25°	
8	8.24	0.0481	Feb. 27, 12 40 p.m.
32	33.62	0.0848	27, 2 15 p.m.
128	133.50	0.1670	Mar. 3, 12 30 p.m.
Alcohol	Sp. cond.	0.000991	Feb. 27, 2 25 p.m.
Alcohol	Sp. cond.	0.000935	Mar. 3, 10 40 a.m.
		35°	
8	8.24	0.05879	Feb. 27, 4 45 p.m.
32	33.62	0.10512	27, 3 45 p.m.
128	133.5	0.20043	Mar. 3, 3 45 p.m.
Alcohol	Sp. cond.	0.001133	Feb. 27, 3 50 p.m.
Alcohol	Sp. cond.	0.00123	Mar. 3, 3 45 p.m.

1, 2, 4 Dihydroxybenzoic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
8	9.99	0.0080	Mar. 24, 11h 00m a.m.
32	33.0	0.0155	24, 11 05 a.m.
128	129.1	0.0171	25, 11 45 a.m.
512	514.9	0.1008	25, 11 50 a.m.
Alcohol	Sp. cond.	0.000551	24, 11 15 a.m.
Alcohol	Sp. cond.	0.000613	25, 11 55 a.m.
		25°	
8	10.06	0.0098	24, 2 30 p.m.
32	33.01	0.0197	24, 2 35 p.m.
128	129.3	0.0272	25, 2 35 p.m.
512	517.5	0.1464	25, 2 40 p.m.
Alcohol	Sp. cond.	0.000631	24, 2 40 p.m.
Alcohol	Sp. cond.	0.000682	25, 2 50 p.m.
		35°	
8	10.10	0.0126	24, 4 20 p.m.
32	33.01	0.0254	24, 4 25 p.m.
128	129.6	0.0391	25, 4 15 p.m.
512	520.2	0.2018	25, 4 20 p.m.
Alcohol	Sp. cond.	0.000735	24, 4 35 p.m.
Alcohol	Sp. cond.	0.000791	25, 4 25 p.m.

1, 2, 4 Dihydroxybenzoic acid—Continued.

Temperature coefficients.

V_m	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct*
8	0.0014	21.9	0.0023	28.3
32	0.004	26.5	0.0054	28.3
128	0.010	59.1	0.0117	43.4
512	0.0445	44.3	0.0539	37.2

Tetrachlorphthalic acid.

V_m	V_c	μ_v	Time of reading.
		15°	
16	16.08	0.0543	Mar. 20, 11h 50m a.m.
64	64.06	0.1011	20, 12 00 m.
256	258.9	0.1294	21, 12 15 p.m.
1024	1027.0	0.3208	21, 12 25 p.m.
Alcohol	Sp. cond.	0.000543	20, 12 05 p.m.
Alcohol	Sp. cond.	0.000554	21, 12 45 p.m.
		25°	
16	16.21	0.0639	20, 12 50 p.m.
64	64.06	0.1198	20, 1 00 p.m.
256	259.3	0.1541	21, 2 00 p.m.
1024	1036.0	0.3860	21, 2 10 p.m.
Alcohol	Sp. cond.	0.000616	20, 12 40 p.m.
Alcohol	Sp. cond.	0.000637	21, 2 15 p.m.
		35°	
16	16.21	0.0770	20, 4 30 p.m.
64	64.06	0.1461	20, 4 30 p.m.
256	260.0	0.1893	21, 4 00 p.m.
1024	1043.0	0.4960	21, 4 10 p.m.
Alcohol	Sp. cond.	0.000711	20, 3 25 p.m.
Alcohol	Sp. cond.	0.000742	21, 4 10 p.m.

Temperature coefficients.

Vm	15° to 25°		25° to 35°	
	Con. unit.	*P. ct.*	*Con. unit.*	*P. ct.*
16	0.0091	16.9	0.0138	18.9
64	0.0187	18.5	0.0262	21.9
256	0.0243	18.1	0.0342	22.5
1024	0.0615	19.3	0.1057	27.6

TABLE 24.—*Changes in concentration.*

Malonic acid.

Time.	Normality.		
	Observed.	Calculated.	Decrease.
			P. ct.
Apr. 16, 12h 45m a.m.	0.1232	0.1250	1.44
16, 2 30 p.m.	0.1229	"	1.68
16, 4 00 p.m.	0.1222	"	2.24
16, 12 50 p.m.	0.03039	0.03125	2.75
16, 2 30 p.m.	0.03008	"	3.75
16, 4 10 p.m.	0.02966	"	5.09
17, 12 00 m.	0.00773	0.007812	1.05
17, 2 30 p.m.	0.00772	"	1.18
17, 4 00 p.m.	0.00771	"	1.31
17, 12 10 p.m.	0.001950	0.001953	0.16
17, 2 40 p.m.	0.001942	"	0.57
17, 4 10 p.m.	0.001930	"	1.18

TABLE 24.—*Changes in concentration*—Continued.

o-Chlorobenzoic acid.

Time.	Normality.		
	Observed.	Calc.	Decrease.
			P. ct.
Mar. 18, 11h 00m a.m.	0.1228	0.1250	1.76
18, 12 15 p.m.	0.1225	"	2.00
18, 4 15 p.m.	0.1210	"	3.20
18, 4 40 p.m.	0.1208	"	3.36
18, 11 00 a.m.	0.03018	0.03125	3.43
18, 11 50 a.m.	0.02976	"	4.77
18, 3 30 p.m.	0.02914	"	6.75
18, 4 30 p.m.	0.02862	"	8.42
19, 11 45 a.m.	0.00772	0.007812	1.18
19, 12 30 p.m.	0.00771	"	1.30
19, 2 30 p.m.	0.00770	"	1.43
19, 4 00 p.m.	0.00769	"	1.56
19, 11 35 a.m.	0.001946	0.001953	0.36
19, 12 30 p.m.	0.001936	"	0.87
19, 2 50 p.m.	0.001932	"	1.08
19, 4 45 p.m.	0.001923	"	1.54

p-Chlorobenzoic acid.

Mar. 26, 12h 30m p.m.	0.0996	0.1250	20.32
26, 2 00 p.m.	0.09919	"	20.65
26, 4 15 p.m.	0.0989	"	20.90
26, 12 40 p.m.	0.0297	0.03125	4.96
26, 2 00 p.m.	0.0292	"	6.55
26, 4 30 p.m.	0.0286	"	8.42
Apr. 1, 12 30 p.m.	0.00771	0.007812	1.31
1, 2 20 p.m.	0.007691	"	1.55
3, 3 30 p.m.	0.00767	"	1.82
3, 4 10 p.m.	0.00766	"	1.95
3, 5 00 p.m.	0.00763	"	2.33
1, 12 35 p.m.	0.001942	0.001953	0.57
1, 3 15 p.m.	0.001923	"	1.54
3, 12 30 p.m.	0.001916	"	1.89
3, 3 30 p.m.	0.001913	"	2.05
3, 4 15 p.m.	0.001903	"	2.57

p-Bromobenzoic acid.

Apr. 28, 11h 30m a.m.	0.12275	0.1250	1.80
28, 2 45 p.m.	0.12129	"	2.97
28, 4 40 p.m.	0.12088	"	3.30
28, 11 40 a.m.	0.03070	0.03125	1.76
28, 2 50 p.m.	0.03007	"	3.78
28, 4 50 p.m.	0.02914	"	6.76
29, 11 00 a.m.	0.00774	0.00781	0.89
29, 12 15 p.m.	0.00773	"	1.02
29, 4 00 p.m.	0.00771	"	1.28
29, 11 10 a.m.	0.001950	0.001953	0.16
29, 12 25 p.m.	0.001932	"	1.08
29, 4 10 p.m.	0.001927	"	1.34

o-Nitrobenzoic acid.

Mar. 23, 12h 15m p.m.	0.12176	0.1250	2.60
23, 12 30 p.m.	0.12088	"	3.30
23, 4 30 p.m.	0.12088	"	3.30
23, 12 30 p.m.	0.03013	0.03125	3.52
23, 2 30 p.m.	0.02914	"	6.75
23, 4 30 p.m.	0.0286	"	8.48
27, 12 00 m.	0.00773	0.00781	1.03
27, 2 30 p.m.	0.00772	"	1.17
27, 4 00 p.m.	0.00771	"	1.29
27, 12 10 p.m.	0.001951	0.001953	0.10
27, 2 40 p.m.	0.001934	"	0.98
27, 4 10 p.m.	0.001928	"	1.28

p-Nitrobenzoic acid.

Time.	Normality.		
	Observed.	Calc.	Decrease.
			P. ct.
Apr. 21, 12h 00m m.	0.03034	0.03125	2.91
21, 2 30 p.m.	0.02976	"	4.77
21, 4 45 p.m.	0.02893	"	7.43
22, 12 00 m.	0.007738	0.007812	0.95
22, 2 30 p.m.	0.007734	"	1.00
22, 4 45 p.m.	0.007721	"	1.17
22, 12 00 m.	0.001950	0.001953	0.16
22, 2 30 p.m.	0.001932	"	1.08
22, 4 30 p.m.	0.001921	"	1.64

1, 2, 4 Dinitrobenzoic acid.

Feb. 27, 12h 30m p.m.	0.1230	0.1250	1.60
27, 2 30 p.m.	0.1213	"	2.96
27, 4 30 p.m.	"	"	2.96
27, 12 20 p.m.	0.02974	0.03125	4.83
27, 4 00 p.m.	"	"	"
27, 5 00 p.m.	"	"	"
Mar. 3, 12 35 p.m.	0.00749	0.007812	4.13
3, 2 30 p.m.	"	"	4.13
[1]4, 10 00 a.m.	0.00764	"	2.20

[1]This titration was made with the solution after it had stood in the cell over night.

1, 2, 4 Dihydroxybenzoic acid.

Mar. 24, 11h 15m a.m.	0.10008	0.1250	19.94
24, 12 30 a.m.	0.09940	"	20.50
24, 2 30 a.m.	0.09899	"	20.82
24, 4 30 a.m.	0.09873	"	21.02
24, 12 25 p.m.	0.03034	0.03125	2.91
24, 12 45 p.m.	0.03029	"	3.08
24, 2 30 p.m.	0.03029	"	3.08
24, 4 30 p.m.	0.03013	"	3.59
25, 12 00 m.	0.00774	0.007812	0.92
25, 2 30 p.m.	0.00773	"	1.03
25, 4 15 p.m.	0.00771	"	1.31
25, 12 10 p.m.	0.00194	0.001953	0.67
25, 2 40 p.m.	0.00193	"	1.18
25, 4 30 p.m.	0.00192	"	1.69

Tetrachlorphthalic acid.

Mar. 20, 11h 50m a.m.	0.06218	0.0625	0.52
20, 12 50 p.m.	0.06168	"	1.32
20, 3 20 p.m.	"	"	"
20, 4 30 p.m.	"	"	"
20, 12 00 m.	0.01561	0.01566	0.32
20 1 00 p.m.	"	"	"
20, 3 30 p.m.	"	"	"
20, 4 30 p.m.	"	"	"
21, 12 15 p.m.	0.00386	0.00391	1.28
21, 2 00 p.m.	0.00385	"	1.53
21, 4 00 p.m.	0.00384	"	1.79
21 12 25 p.m.	0.000973	0.000976	0.31
21, 2 10 p.m.	0.000965	"	1.13
21, 4 10 p.m.	0.000958	"	1.85

DISCUSSION OF RESULTS.

It will be noted in tables 23 and 24 that 1, 2, 4 dinitrobenzoic acid shows irregularity in titration values. The conductivity of this acid was determined before we began to keep the solutions used in titrating at a constant temperature. With all other acids the results show that with increase in time a greater amount of esterification has taken place; that is, the normality of the acid has become less. The amount of ester formed in a given time depends upon the nature of the acid.

Since each dilution was made up independently of the others, that is, by direct weight, it is interesting to note that the proportion of ester formed in the less dilute solutions is much greater than in the more dilute. Indeed, in some cases there is practically no ester formed in the $\frac{n}{128}$ and $\frac{n}{512}$ solutions.

As has already been stated, none of the conductivities is greater than unity; and, consequently, the molecular conductivity of the alcohol for each dilution is relatively quite large, the correction for this factor being in some cases as much as 70 per cent of the total conductivity. It can be seen from the tables that the conductivity of the alcohol alone varies considerably, usually increasing appreciably with time. Some of the conductivities of the alcohol increase with rise in temperature, some actually decrease, while others remain very nearly constant. We can offer no explanation for this lack of uniform variation, except to call attention to the several factors which might affect the conductivity of the pure solvent. One might be the absorption by the alcohol of traces of various gases or water-vapor from the atmosphere. This, however, ought to be a negligible factor, since our cells were very nearly filled and were tightly closed with ground-glass stoppers.

The decomposition effects brought about by the platinum electrodes may be an important factor. (Compare here the work of Wildermann and others on this question.) It is evident that the electrodes do have some effect, since fresh alcohol just taken from the bottle does have a fairly uniform conductivity. Part of the effect with alcohol which stood in the cell over night might be due to the solubility of the glass cells. This, however, is not at all probable, since our cells have been in constant use in this laboratory for three years, and hard glass is not very soluble in alcohol.

The conductivities of some of the solutions, and curiously enough of the more dilute solutions, vary to a much smaller extent, with time, than does the conductivity of the pure alcohol.

It will be recalled that Wakemann plotted curves of conductivity of the organic acids against percentage alcohol (see fig. 21), and on extending the curves in the direction of 100 per cent alcohol they apparently approached zero conductivity as a limit. As can be seen from our results, the conductivities do not actually approach zero, but a number less, and usually very much less than unity.

One of the most interesting facts developed in this work is the very large percentage temperature coefficients of conductivity of the organic acids in alcohol. These range for 10° from 15 to 50 per cent.

There is often a rapid increase in the conductivity of the organic acids with increase in dilution, yet certain of the acids behave in just the opposite manner—e. g., *o*-chlorbenzoic acid and *p*-nitrobenzoic acid.

Our results seem to suggest the following possibilities, if we take into account the work done here on the organic acids in aqueous solutions; that there is much greater alcoholation than hydration, and this is decreased with rise in temperature. The work already done in this laboratory renders this highly improbable. The alcoholates may be more unstable with rise in temperature than the hydrates, but water seems to have in general far more power to combine with dissolved substances than alcohol.

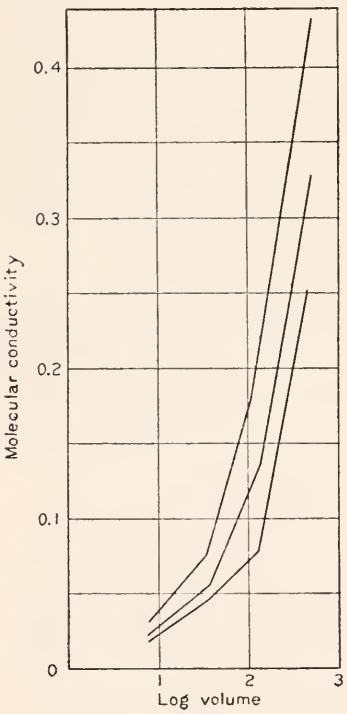


FIG. 25.—Malonic acid.

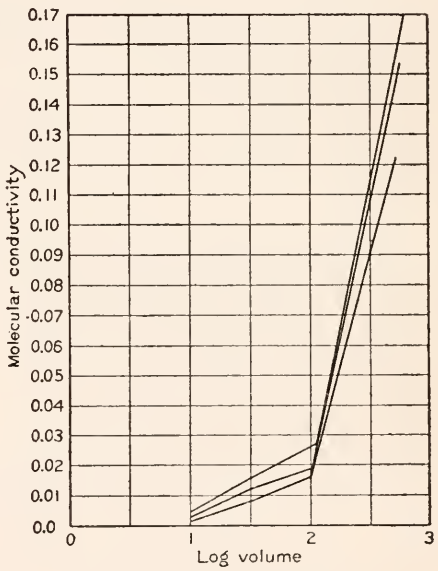


FIG. 26.—*p*-Chlorobenzoic acid.

If dissociation in alcoholic solutions increases with rise in temperature, it might account for the large temperature coefficients of conductivity in such solutions; but this again seems highly improbable. The greater expansion of the alcohol with rise in temperature would allow a freer movement of the ions, and this doubtless is of some significance.

A method for determining the dissociation of the organic acids in alcohol (somewhat similar to that used with aqueous solutions) will, it is hoped, be worked out in the investigation of this subject which is to follow this preliminary one. It will involve the study in alcohol of

the conductivity of some salts of the acids, as well as of hydrochloric acid and the chlorides corresponding to these salts.

The increase in conductivity with increase in volume is shown graphically in figures 25 and 26. The increase in conductivity with rise in temperature can be seen from figs. 27 and 28. In the latter case the curves have very much the appearance of those in aqueous solutions. This suggests that perhaps the increase in molecular conductivity in alcohol with rise in temperature is a parabolic function, as in aqueous solutions, and that the Euler equation, $\mu_v = \mu_0 + at - bt^2$, applies to both.

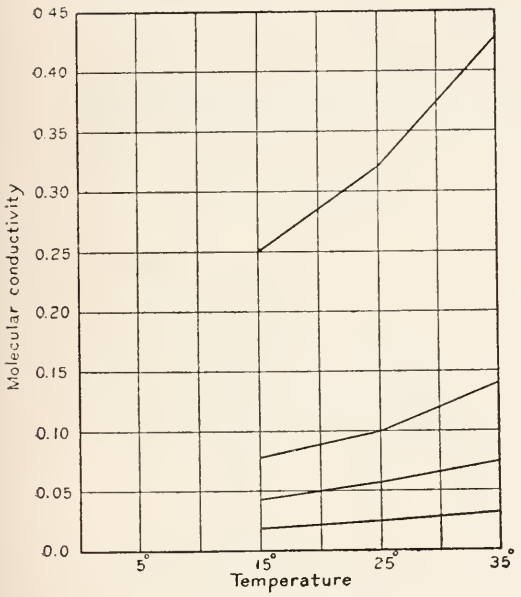


FIG. 27.—Malonic acid.

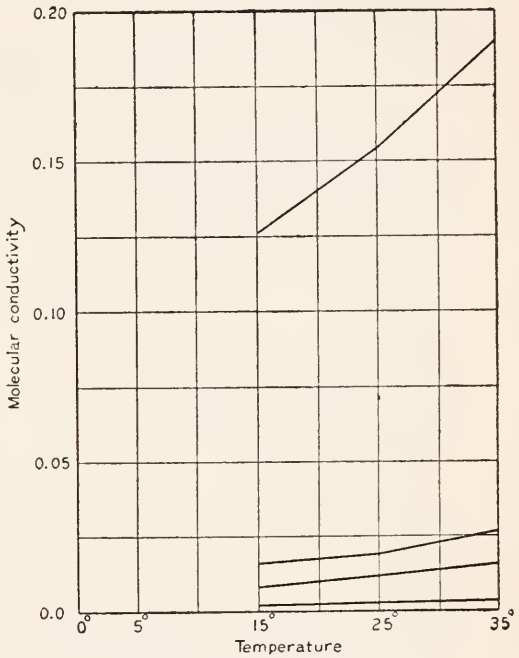


FIG. 28.—*p*-Chlorobenzoic acid.

This will be tested in the later work by determining the conductivities of some of the acids at temperatures other than the three already named, and comparing the results obtained. The most striking feature of the conductivities of the same acids in water is their very small value. When we consider the relative powers of alcohol and water to dissociate salts, the above fact does not at present seem to admit of any very satisfactory explanation. Alcohol has from one-fourth to one-fifth the dissociating power of water, as shown by their dissociation of salts. With the organic acids the conductivities in alcohol are often *several hundred times smaller than in water*. It is hoped that the further work which is now in progress in this laboratory on this problem may throw some light on this relation.

CHAPTER IV.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF POTASSIUM IODIDE AND SODIUM IODIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER.

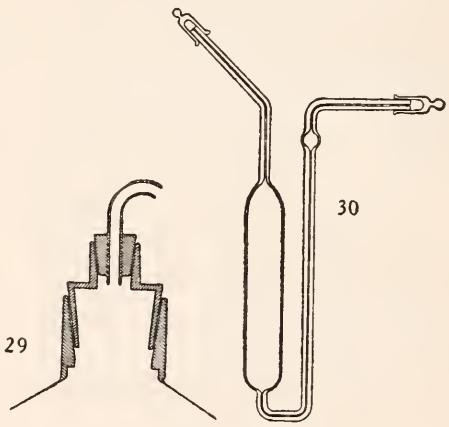
By E. P. Wightman, P. B. Davis, and A. Holmes.

A brief review of the conductivity and viscosity work in non-aqueous and mixed solvents, during the past twelve years, is contained in the last chapter of this monograph.[1] All discussion of this work can, therefore, be omitted here.

EXPERIMENTAL.

PURE ANHYDROUS ALCOHOL.

Pure anhydrous alcohol was obtained in the following manner: The ordinary 95 per cent ethyl alcohol was heated for three days with lime in a copper vessel connected with a reflux condenser. A cooling coil in the neck of the vessel brought about rapid condensation, thus acting as a safety device, so that there was no danger in keeping the alcohol constantly heated during the day without close attention.



Figs. 29 and 30.

In distilling the alcohol, a block-tin condenser connected with the copper vessel by means of a ground-brass joint (see fig. 29) was used. In this way the ordinary cork stopper was avoided, and the alcohol vapor came in contact only with a metal surface before being condensed. The distillate was received into large (glass-stoppered) Jena glass bottles.

Specific-gravity determinations showed this to contain from 0.1 per cent to 0.07 per cent of water. It was, therefore, heated a second time for three or four days with fresh lime and then redistilled. The distillate obtained in this manner had a specific gravity from about 0.78511 to 0.78516, usually nearer the former value, which corresponds to a percentage of 99.98 per cent alcohol.

SPECIFIC-GRAVITY DETERMINATIONS.

Special care was taken in the determination of densities. Two pycnometers (fig. 30), very nearly alike, were used in the case of

[1] See also Carnegie Inst. Wash. Pubs. Nos. 80 and 180.

pure alcohol. They were similar in shape to those employed in earlier work, but were nearly twice as large, having a volume capacity somewhat over 20 c.c., and the capillary was of 0.5 mm. bore. By using one of these as a tare against the other, effects caused by changes in atmospheric conditions were avoided. It may be said here also that in all weighings the load was weighed on each end of the balance beam, and that the final weight represented the mean value of the two. For all other specific-gravity determinations smaller pycnometers with capacities of about 10 c.c., were employed, and were weighed directly, as in the previous case, on each end of the beam.

Corrections were always applied to the apparent weights of the contents of the pycnometers in order to reduce them to the vacuum standard. For this purpose a record was kept of the height of the barometer and the temperature of the balance-room at the time of weighing. The buoyancy correction was afterwards determined by means of table 22, page 37 of Circular No. 19 of the Bureau of Standards. The capacities of the pycnometers were found in the usual manner, with the addition of the corrections just mentioned, at 15°, 25°, and 35° C. Moreover, the pycnometers were reset and reweighed twice at each temperature, in order to be sure that the capacities were correct.

MIXED SOLVENTS.

The mixed solvents were made up in percentages by weight of alcohol and water. These percentages were found from the density tables on pages 6 and 7 of Circular No. 19 of the Bureau of Standards. The making of the mixtures of alcohol and water on a weight basis was by a volume method, according to the following formula:

$$\frac{md'(p-x)}{xd}=y$$

m being the number of cubic centimeters of alcohol of density d'; p, the absolute percentage of alcohol; x, the desired percentage of alcohol to be obtained; d, the density of the water used; y, the number of cubic centimeters of water of density d to give the required percentage of alcohol. The formula in practice was simplified by taking 100 c.c. of the alcohol and calculating a table, using several temperatures as ordinarily met with in the laboratory (each degree from 20° to 25°).

The above formula is derived in the following manner:

Let k = the absolute weight of the alcohol taken; then $k = md'p'$, where p' is the fraction of alcohol in the absolute alcohol taken.

$\frac{k}{x}(100-x)$ = weight of water to be added to make x per cent alcohol; whence

$$\frac{k}{x}(100-x)=md'(1-p')+yd$$

where $md'(1-p')$ is the amount of water in the alcohol and yd the amount of water to be added to make the amount $\frac{k}{x}(100-x)$.

Substituting for k, $md'p'$, the expression becomes

$$\frac{md'p'(100-x)}{x} = md'(1-p') + yd \text{ or } \frac{md'(100\,p'-x)}{xd} = y$$

If p' is in percentage this becomes

$$\frac{md'(p-x)}{xd} = y$$

In this connection a question arose as to whether or not the volume method of making up the solvent was experimentally accurate. On the face of it the gravimetric method appears to be a safer one, but it is also much longer and more tedious. A test was therefore made of both methods. The calculated amounts of water and alcohol, that is, the apparent weights of the two necessary to give a 50 per cent mixture by weight (in vacuo), were weighed into a glass-stoppered flask and thoroughly mixed. A density determination of the mixture was made at 25° and found to be 0.909826, or 50.01 per cent alcohol.

In like manner a mixture was made up by volume, using the quantities of alcohol and water calculated from the above formula necessary to make a 50 per cent mixture by weight; the specific gravity in this case being 0.90980, corresponding to 50.02 per cent alcohol.

DISSOLVED SALTS.

Sodium iodide and potassium iodide were used in this investigation. They were obtained from Kahlbaum and were extra pure material. In fact, it was not even necessary for us to recrystallize them. We analyzed them, ground them fine, and placed them in a desiccator to dry them thoroughly before weighing.

Potassium iodide is not very soluble in pure alcohol. It was with great difficulty that we were able to make a N/8 solution of it in the 95 per cent alcohol.

PIPETTES.

25 c.c., 50 c.c., 100 c.c., 150 c.c., and 200 c.c. pipettes, carefully calibrated by weighing the water they would deliver, were employed, together with a 10 c.c. graduated pipette, for making up the mixed solvents.

CONDUCTIVITY CELLS.

The conductivity cells were of the same type as those used here for such work. The general method of determining conductivity previously described[1] was also employed. Since a number of changes in the temperature regulation, which will be spoken of later, were made at the beginning of this work, and since these changes necessitated rewiring of the system for the determining of conductivity, we tested

[1]Amer. Chem. Journ., **46**, 56 (1911).

this system very thoroughly to be sure that all external resistance in the circuit was negligible, or, when it was not, we determined its exact magnitude in order to make the proper corrections.

The system of wiring was a double one, so that by means of a double-throw, double-blade switch, both a and b in the formula for calculating conductivity

$$\mu_v = K\frac{va}{Wb}$$

could be read directly on the bridge. If two standard resistance boxes are connected one to each side of the bridge, and plugs representing equal resistances are removed from both boxes, then the reading of the wire will be 500 mm., or exactly its middle-point; provided, of course, that there is no appreciable resistance in the circuit itself (if there is it must be evenly balanced). Such was the case with our equipment. Therefore, there were no corrections of this kind to be made to a or b in the conductivity determinations.

But this double system also serves another purpose. When the conductivity of a solution is being measured, if both a and b are read on the bridge wire for the same resistance—supposing that all other conditions remain constant—then the mean of the two readings will be 500 mm. If we do not find by actual experiment that our mean value is 500 mm., we may be sure that at least one of the other conditions, such as, for example, temperature, is varying and needs attention.

It was very difficult in some of the measurements to obtain distinct minima. The distances covered on the wire on either side of the minimum point in such instances, were so great before finding corresponding sounds on the two sides that the minimum point itself could be only approximated. We endeavored to overcome this difficulty by connecting a condenser in parallel with the rheostat. In determining the conductivities of the alcohol and alcohol-water solutions, it was practically useless; the fact is, the condenser actually made the readings in some cases harder to obtain. However, in determining the cell constants of those cells which required low resistances, the bridge readings were made much sharper over a shorter distance, and the minimum very much more distinct by the use of the condenser. We did not arrive at any general conclusion concerning its use.

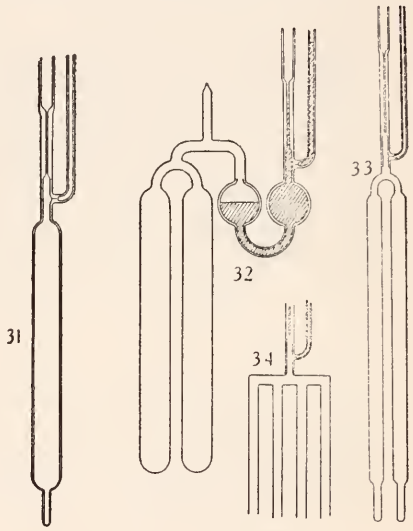
TEMPERATURE REGULATORS.

A number of different types of thermo-regulators have been used in this laboratory from time to time; of the earlier forms it is not necessary to speak. The regulators used during the last two or three years have had the general form of that shown in figure 31, and were filled with mercury.

At the beginning of this investigation we devised a regulator (fig. 32) in which only the trap bulbs and capillary contained mercury, the series

of tubes (we used only two, figure 32) being filled with toluene, which has about 6 times the cofficient of expansion of mercury. Instead of using a 0.75 mm. capillary, into which a platinum wire connecting with the regulating circuit was introduced, as in the old mercury regulator, a capillary tubing of 2 mm. internal bore was employed, and the contact was made by means of a steel wire of about 1.5 mm. diameter and rounded at the end. The regulator worked with a fairly high degree of accuracy, having a total variation of only 0.01° at 25° and lower temperatures; and for a time it worked fairly well at 35°, but it did not prove to be satisfactory for any length of time at the latter temperature. One difficulty was that the mercury at the surface of the glass sooner or later became covered with toluene, and this began to creep out, especially when the regulator was not kept constantly at the desired temperature, but was allowed to cool down over night.

This question in the meantime suggested itself: Why is it not possible to have two or more long tubes of thin glass containing mercury instead of toluene, and in order to avoid too great a weight, to have these tubes of narrow bore? Thus, we would have a greatly increased surface of mercury, in comparison with the old form of regulator, and therefore a greater expansion. (See figs. 33 and 34.) Such a form was tried with great success.



FIGS. 31, 32, 33, and 34.

The supply of heat to the thermostat was controlled by a gas-regulator consisting of a 150-ohm relay, connected electrically with the thermo-regulator and having an arrangement attached directly to the armature, for cutting off the gas.

CORRECTIONS FOR EXPANSION AND CONTRACTION.

When the conductivities of electrolytes in water as a solvent are determined at the temperatures at which we worked—that is, 15°, 25°, and 35°—when the solutions are made up at 20°, the change in volume caused by the expansion or contraction of the solvent and solutions between 20° and these temperatures is so small that the volume correction can be neglected. With alcohol and mixtures of alcohol and water, however, this is not the case. The expansion here is very appreciable, and there are, in consequence, changes in the normality of the solutions for which corrections should be made.

The proper corrections have been applied to the data in the following tables. The difference between the density at 20° and at the other temperature in question was determined. This difference represents the decrease or increase in volume per cubic centimeter of the solution. Subtracting the decrease below 20° from 1.0 and adding it to 1.0 above 20°, gives the coefficient of contraction or expansion respectively. Since at 15° the volumes of the solutions become smaller, there is a decrease also in the molecular conductivities. At 25° and 35° the expansion, bringing about an increased volume normality, results in a positive correction to the conductivity.

VISCOSITIES.

The viscosity apparatus used in this investigation was essentially the same as that described by Davis and Jones[1] in their work on glycerol. The viscosimeters were of the general type therein described, the capillary tubes having a diameter of about 0.5 mm. Some improvements were made in connection with the constant-pressure apparatus for elevating the liquid to the upper mark on the capillary limb of the viscosimeter, and special precautions were taken to dry the air thoroughly by passing it through a long drying-tube filled with calcium chloride. By means of dust-traps filled with cotton, clogging of the capillary was effectively prevented.

The desk supporting the viscosimeter stand was not connected with the supports for the motor and stirrers. This was to avoid the vibration due to the motor, and was secured by attaching the motor support directly to the walls of the building. To reduce the vibrations still further, the stand holding the viscosimeter rested on several layers of felt.

The stand itself consisted of a heavy tripodal base, with a three-quarter-inch bronze standard, to which a heavy horizontal arm was attached by means of a set-screw. The viscosimeters were fastened to the arm by means of a spring clamp, the tension of which was adjusted by a thumb-screw. The stand was carefully leveled by means of leveling screws, at right angles to the line of sight in reading the viscosimeter. Leveling in the other direction was accomplished by sighting along the vertical arm of the viscosimeter to a plumb-line suspended before the glass window in the bath.

Temperature regulation in the viscosity work was essentially the same as that in the conductivity. By means of the mercury regulator (fig. 34) already described, the temperature was kept constant for any desired length of time to within 0.01° at 15° and 35°, and to within 0.005° at 25°.

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[1]Zeit. phys. Chem., **81**, 68 (1912).

TABLE 25.—*Viscosity and fluidity of potassium iodide in alcohol-water mixtures.*

Temp.	Molecular concentration.	100 per cent.		95 per cent.		90 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	.....	.....	0.01605	62.32	0.01724	58.04
	Solvent...	.....	.....	0.01450	68.97	0.01674	59.70
25°	N/8.....	.....	.....	0.01298	77.08	0.01370	72.99
	Solvent...	.....	.....	0.01183	84.55	0.01514	76.12
35°	N/8.....	.....	.....	0.01070	93.46	0.01098	91.14
	Solvent...	.....	.....	0.00971	103.00	0.01044	95.81

Temp.	Molecular concentration.	80 per cent.		70 per cent.		60 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	0.02247	44.49	0.02703	37.00	0.03015	33.16
	Solvent...	0.02205	45.36	0.02625	38.12	0.03039	32.90
25°	N/8.....	0.01882	53.14	0.01990	50.25	0.02171	46.06
	Solvent...	0.01679	59.60	0.01913	52.28	0.02169	46.10
35°	N/8.....	0.01331	75.13	0.01514	66.05	0.01608	62.22
	Solvent...	0.01297	77.13	0.01428	70.06	0.01609	62.18

Temp.	Molecular concentration.	50 per cent.		40 per cent.		30 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	0.03269	30.59	0.03358	29.78	0.03114	32.11
	Solvent...	0.03293	30.37	0.03427	29.18	0.03177	31.49
25°	N/8.....	0.02294	43.60	0.02474	40.43	(0.02127)	47.12
	Solvent...	0.02264	44.18	0.02328	42.96	0.02115	47.28
35°	N/8.....	0.01676	59.67	0.01675	59.70	0.01525	65.61
	Solvent...	0.01625	61.55	0.01662	60.17	0.01599	62.57

Temp.	Molecular concentration.	20 per cent.		10 per cent.		5 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	0.02492	40.13	0.01693	59.06	0.01389	72.05
	Solvent...	0.02566	38.98	0.01727	57.96	0.01410	70.92
25°	N/8.....	0.01752	57.09	0.01255	79.72	0.01063	94.07
	Solvent...	0.01786	56.03	0.01270	78.74	0.01073	93.20
35°	N/8.....	0.01287	77.70	0.00969	103.2	0.00841	118.9
	Solvent...	0.01291	77.46	0.00975	102.6	0.00847	118.1

Viscosities at any temperatures were calculated from the formula

$$\frac{\eta}{\eta_0} = \frac{st}{s_0 t_0}$$

where η is the viscosity coefficient desired; η_0 the absolute viscosity of water at the desired temperatures; s_0 the specific gravity of water at that temperature, and t_0 the time of flow of water in any given viscometer. s and t are, respectively, the density of the solution and its time of flow in the same viscosimeter.

The fluidity is the reciprocal of the viscosity, $\phi = \frac{1}{\eta}$

The percentage temperature coefficients of fluidity are derived in the same manner as those of conductivity.

TABLE 26.—*Temperature coefficients of fluidity of potassium iodide in alcohol-water mixtures.*

Per cent alcohol.	15 to 25°		25 to 35°	
	N/8 KI	Solvent.	N/8 KI	Solvent.
100....	.....	.....	.....	.....
95....	0.0237	0.0226	0.0213	0.0217
90....	0.0257	0.0275	0.0249	0.0259
80....	0.0194	0.0309	0.0338	0.0277
70....	0.0358	0.0374	0.0334	0.0341
60....	0.0386	0.0401	0.0351	0.0349
50....	0.0425	0.0455	0.0368	0.0395
40....	0.0358	0.0468	0.0476	0.0401
30....	0.0467	0.0501	0.0392	0.0324
20....	0.0422	0.0437	0.0361	0.0382
10....	0.0349	0.0359	0.0295	0.0304
5....	0.0306	0.0314	0.0265	0.0267

TABLE 27.—*Viscosity and fluidity of sodium iodide in alcohol-water mixtures.*

Temp.	Molecular concentration.	100 per cent.		95 per cent.		90 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	0.01427	70.21	0.01658	60.33	0.01845	54.22
	Solvent...	0.01292	77.45	0.01530	65.36	0.01767	56.64
25°	N/8.....	0.01191	83.98	0.01334	75.01	0.01471	67.98
	Solvent...	0.01054	94.88	0.01227	81.51	0.01392	71.85
35°	N/8.....	0.00981	101.9	0.01087	92.00	0.01172	85.34
	Solvent...	0.00871	114.8	0.00993	100.7	0.01100	90.91

Temp.	Molecular concentration.	80 per cent.		70 per cent.		60 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	0.02282	43.78	0.02692	37.15	0.03088	32.38
	Solvent...	0.02232	44.80	0.02634	37.96	0.03049	32.81
25°	N/8.....	0.01738	57.54	0.01988	50.31	0.02209	45.29
	Solvent...	0.01701	58.29	0.01916	52.25	0.02175	45.99
35°	N/8.....	0.01342	74.52	0.01500	66.67	0.01627	61.48
	Solvent...	0.01316	76.01	0.01437	69.61	0.01599	62.57

Temp.	Molecular concentration.	50 per cent.		40 per cent.		30 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	0.03309	30.22	0.03372	29.65	0.03145	31.80
	Solvent...	0.03333	30.00	0.03421	29.23	0.03165	31.60
25°	N/8.....	0.02308	43.34	0.02302	43.44	0.02130	46.95
	Solvent...	0.02315	43.20	0.02318	43.15	0.02112	47.35
35°	N/8.....	0.01676	59.67	0.01649	60.66	0.01521	65.75
	Solvent...	0.01662	60.17	0.01643	60.87	0.01494	66.97

Temp.	Molecular concentration.	20 per cent.		10 per cent.		5 per cent.	
		η	φ	η	φ	η	φ
15°	N/8.....	0.02492	40.13	0.01739	57.57	0.01406	71.16
	Solvent...	0.02551	39.20	0.01752	57.09	0.01410	90.92
25°	N/8.....	0.01722	58.09	0.01288	77.69	0.01073	93.20
	Solvent...	0.01766	56.67	0.01288	77.69	0.01072	93.28
35°	N/8.....	0.01259	79.50	0.00987	101.3	0.00849	117.8
	Solvent...	0.01296	77.19	0.00982	101.8	0.00847	118.1

TABLE 28.—*Conductivity of potassium iodide in mixtures of ethyl alcohol and water.*

Per cent alcohol.	V = N/8 at 20°						Per cent alcohol.	V = N/128 at 20°.					
	15°		25°		35°			15°		25°		35°	
	v	μ_v	v	μ_v	v	μ_v		v	μ_v	v	μ_v	v	μ_v
0.00	.....	.....	8.000	120.7	8.000	144.50	4.98	127.88	90.09	128.26	113.37	128.56	138.29
4.98	7.993	83.25	8.010	104.06	8.035	126.30	10.02	127.85	75.72	128.28	97.43	128.64	121.46
9.55	7.990	70.87	8.011	90.44	8.039	111.64	20.00	127.74	54.23	128.39	73.18	128.93	94.69
20.00	7.984	49.67	8.018	66.46	8.058	85.07	21.75	127.71	51.06	128.41	69.59	128.99	90.38
30.06	7.976	38.39	8.025	52.78	8.086	69.15	30.06	127.61	41.70	128.50	57.50	129.25	76.17
40.23	7.971	32.34	8.030	44.49	8.091	58.44	40.23	127.53	35.72	128.58	49.98	129.46	66.58
50.61	7.966	30.28	8.032	41.07	8.099	53.34	50.26	127.49	32.80	128.61	45.15	129.56	59.60
60.70	7.966	26.49	8.034	35.15	8.101	45.00	60.34	127.48	30.74	128.63	41.39	129.62	53.88
71.09	7.960	24.27	8.034	31.46	8.101	39.54	70.42	127.46	29.85	128.63	39.17	129.66	49.52
80.95	7.964	23.22	8.035	29.27	8.104	36.02	80.51	127.45	29.60	128.65	36.92	129.67	46.20
92.63	7.962	19.76	8.035	23.77	8.104	28.28	90.67	127.45	29.05	128.66	35.88	129.69	43.48
96.09	7.966	18.63	8.035	22.22	8.108	26.12	95.77	127.45	28.59	128.65	34.61	129.67	40.37

TABLE 29.—*Conductivity of sodium iodide in mixtures of ethyl alcohol and water.*

Per cent alcohol.	V = N/8 at 20°						Per cent alcohol.	V = N/32 at 20°					
	15°		25°		35°			15°		25°		35°	
	v	μ_v	v	μ_v	v	μ_v		v	μ_v	v	μ_v	v	μ_v
0.00	8.000	81.00	8.000	100.4	8.000	121.6	0.00	.....	.....	32.00	107.40	32.00	130.60
4.98	7.993	65.66	8.010	83.03	8.035	101.78	4.98	31.97	69.11	32.04	87.75	32.14	108.70
10.02	7.991	55.09	8.011	71.28	8.040	89.06	10.02	31.96	58.20	32.04	75.61	32.16	95.08
20.00	7.984	39.62	8.018	53.62	8.058	69.47	20.00	31.93	41.90	32.07	57.12	32.23	74.50
21.75	7.982	37.48	8.019	51.10	8.062	66.54	30.06	31.90	31.98	32.10	44.58	32.31	60.32
30.06	7.976	30.82	8.025	42.89	8.078	56.69	40.23	31.88	28.56	32.12	40.09	32.36	53.54
40.23	7.971	26.91	8.030	37.49	8.091	49.69	50.26	31.87	25.33	32.13	35.04	32.39	47.10
50.26	7.968	24.66	8.032	33.73	8.097	44.21	60.34	31.87	25.23	32.13	33.97	32.40	44.18
60.34	7.967	23.09	8.033	30.99	8.101	39.97	70.42	31.86	23.83	32.14	31.36	32.42	40.25
70.42	7.966	22.00	8.034	28.70	8.104	36.41	80.51	31.86	24.15	32.14	30.71	32.42	38.31
80.51	7.966	20.78	8.035	26.39	8.105	32.64	90.67	31.86	23.47	32.14	28.69	32.42	34.90
90.67	7.966	19.42	8.035	23.80	8.106	28.63	95.77	31.86	22.12	32.14	26.85	32.42	32.04
95.77	7.966	18.18	8.034	21.88	8.105	25.95							
99.98	7.966	16.51	8.034	9.471	8.103	22.68							

Per cent alcohol.	V = N/128 at 20°						Per cent alcohol.	V = N/1024 at 20°					
	15°		25°		35°			15°		25°		35°	
	v	μ_v	v	μ_v	v	μ_v		v	μ_v	v	μ_v	v	μ_v
0.00	128.00	112.5	128.00	112.50	128.00	136.80	0.00	1024.0	.....	1024.0	116.40	1024.0	141.6
4.96	127.88	73.31	128.26	92.96	128.56	114.81	5.06	1023.0	77.89	1025.3	98.87	1028.5	121.9
10.00	127.85	61.26	128.28	79.83	128.64	100.39	10.02	1022.8	65.56	1025.4	85.44	1029.1	107.6
20.00	127.74	44.13	128.39	60.18	128.93	78.35	20.00	1021.9	46.84	1026.3	63.86	1031.5	83.7
29.98	127.61	32.83	128.50	46.09	129.25	61.83	30.06	1020.9	34.81	1027.2	48.97	1034.0	65.8
39.98	127.53	29.67	128.58	41.81	129.46	56.02	40.23	1020.3	31.72	1027.8	44.62	1035.6	60.2
50.02	127.49	26.79	128.61	34.98	129.56	48.04	60.34	1019.8	30.38	1028.2	40.69	1036.9	53.5
63.23	127.48	24.82	128.63	36.07	129.62	43.42	70.42	1019.7	28.51	1028.4	37.83	1037.3	48.7
70.06	127.46	25.99	128.63	34.42	129.66	44.32	80.51	1019.6	30.42	1028.4	39.02	1037.4	49.5
80.52	127.45	27.07	128.65	34.76	129.67	43.71	90.67	1019.6	31.83	1028.5	38.39	1037.5	48.7
90.61	127.45	27.27	128.66	33.79	129.69	41.28	95.77	1019.6	30.70	1028.4	36.46	1037.4	45.8
95.00	127.45	26.10	128.65	31.88	129.67	38.40							

DISCUSSION OF THE RESULTS.

VISCOSITY AND FLUIDITY.

Viscosity data have been obtained in the various mixtures of alcohol and water that have been studied, both for the solvents and the N/8 solutions of potassium and sodium iodides. The values for the more dilute solutions approach those for the solvents too closely to be accurately differentiated from them. The results are given in tabular form, together with a representative table of temperature coefficients for the range of temperature over which the work was carried out, *i. e.*, 15°, 25°, and 35°.

Table 25 gives the values found for potassium iodide, and table 27 similar values for sodium iodide. It will be seen that the effect of these salts on the viscosity of alcohol-water mixtures is comparatively small for the N/8 solutions. In no instance does the decrease in fluidity, which corresponds to an increase in viscosity, exceed a few per cent, and in certain of the mixtures containing the smaller percentage of alcohol a marked increase in the fluidity is to be noted. This will be discussed when each salt is taken up separately.

In all mixtures of alcohol and water from 100 per cent alcohol to that containing 60 per cent alcohol, both potassium and sodium iodides show a marked increase in the viscosity of the solvents at the temperatures studied. Beyond this point the effect on the viscosity is somewhat different for each salt.

From the 60 per cent solvent down to the 0 per cent, *i. e.*, pure water, potassium iodide *lowers the viscosity of the solvent* to an appreciable extent at 15°. At 25° no negative viscosity effect is to be noted until the 30 per cent mixture is reached. At this point a corresponding decrease was also noted at 35°. Potassium iodide, therefore, may be said to increase the viscosity of all mixtures of alcohol and water from 100 per cent alcohol to 30 per cent alcohol at 25° and 35°, and to decrease the viscosity of all the other mixtures up to and including pure water.

The shifting of the point at which the fluidity curve for the salt crosses that for the solvent is to be accounted for by the change in association of the solvent with rise in temperature. Since a rise in temperature causes a breaking down of the molecular aggregates of the solvent giving ultimate particles of smaller volumes, it follows that this would tend to shift the transition-point towards one extreme or the other. Since potassium iodide increases the viscosity of mixtures containing a high percentage of alcohol, the shifting takes place towards the water end of the curve.

The points discussed above are shown graphically by figures 35 and 36, which represent the curves for solvent and solutions at 15° and 25°. Table 26 contains the temperature coefficients of fluidity for the solvent and N/8 potassium iodide, for all percentages of alcohol and water studied. They are seen to decrease in value with rise in temperature

and have a maximum at about the 30 per cent alcohol mixture. The values for the solvent are slightly higher than those for the solution.

Sodium iodide, like potassium iodide, increases the viscosity of mixtures containing a higher percentage of alcohol. At 15° the transition-point occurs in the neighborhood of the 50 per cent mixture. At 25° and 35° somewhat irregular results were noted. The salt increases the viscosity of all the solvents through the 50 per cent mixture. Beyond that point an apparently periodic effect occurs, negative viscosity appearing only in the 40 per cent and 20 per cent mixtures. Reference to the tables will show that the difference between solution

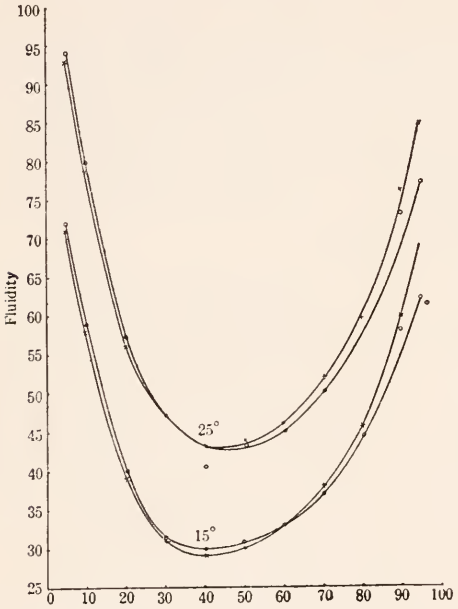


FIG. 35.—Fluidity of KI at 15° and 25°.

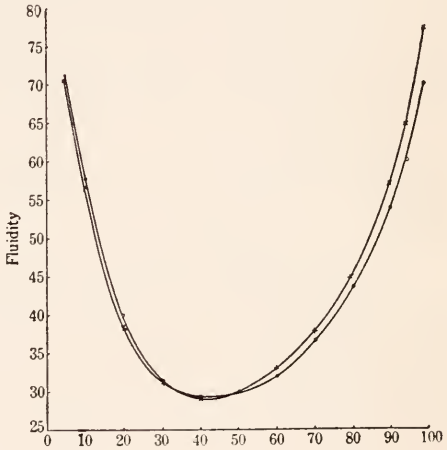


FIG. 36.—Fluidity of NaI at 15°.

and solvent is very small for the N/8 concentration. In the 10 per cent and 5 per cent mixtures the salt exerts scarcely any effect on the solvent at 25° and 35°.

From this it would seem that the molecular volume of the dissolved sodium iodide is smaller than either the associated alcohol or water complexes; but in mixtures of these two solvents in which the association becomes smaller, a negative viscosity effect is apparent as soon as the dissolved particles are larger than the ultimate particles of the solvent. From the data at hand the change in association appears to take place more largely in the case of the water than of the alcohol. Similar reasoning holds for potassium iodide.

The explanation of the phenomenon of negative viscosity as first offered by Veazey[1], has been further elaborated by subsequent in-

[1]Amer. Chem. Journ., **37**, 405 (1907).

vestigators[1] and it is unnecessary to discuss it here in detail. It is sufficient to state that the facts brought out in this investigation are entirely in harmony with the theories established by previous workers.

CONDUCTIVITY.

The conductivity data given above were plotted in the form of curves; ordinates representing conductivities and abscissas the percentages by weight of alcohol. The conductivity of each concentration of the solutions at the three temperatures were plotted on one curve sheet in order the better to compare them. Before plotting these curves we attempted to plot one which would give us the conductivity values (plotting conductivity against normality) for the ordinary normalities

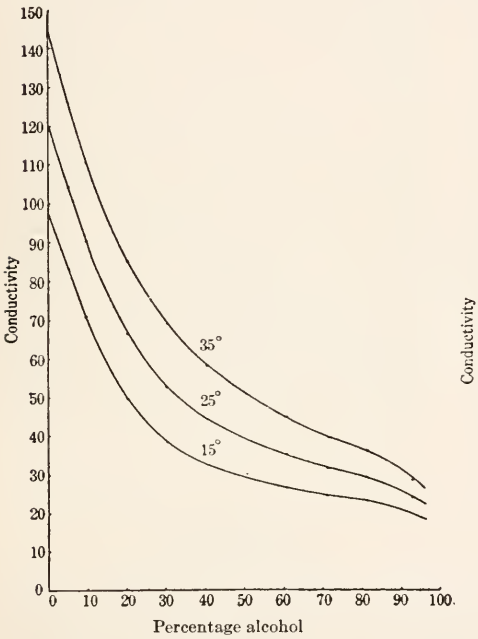


FIG. 37.—N/8—KI.

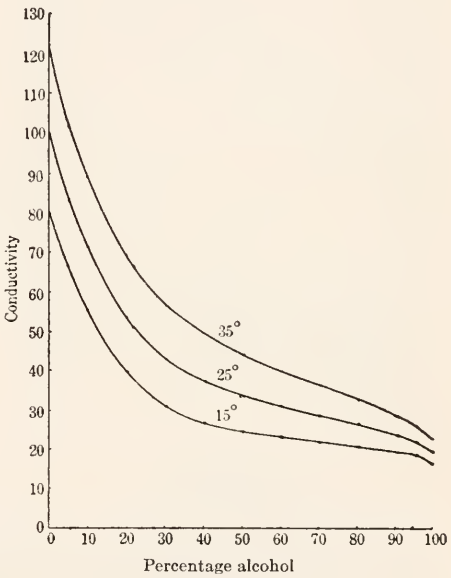


FIG. 38.—N/8—NaI.

N/8, N/32, etc., instead of for those given above. However, we found this to be impracticable, both as to the drawing of the curves and also as to the results we would have obtained; since, with reference to the latter, the slight change in conductivity that would result would not be sufficient to alter, to any appreciable extent, the character of the curves obtained by using the above values, although these values are obviously not *strictly* comparable with one another.

It will be seen from figures 37 and 38, which show the curves for N/8 potassiu n and sodium iodides at 15°, 25°, and 35°, that there is a continual decrease in the conductivity of both salts in passing from the pure water to the pure alcohol.

[1]Carnegie Inst. Wash. Pub. No. 80.

The values for pure-water solutions were taken from the work of West and Jones,[1] except those for 15°. For this temperature they were calculated by means of the equations

$$\mu_t = 55.26 + 1.581t + .00898t^2$$

for sodium iodide, and

$$\mu_t = 68.45 + 1.883t + .00829t^2$$

for potassium iodide. These equations apply only to the N/8 solutions, every other dilution requiring a different equation. The accuracy with which West and Jones's values fit the curve is worth noting.

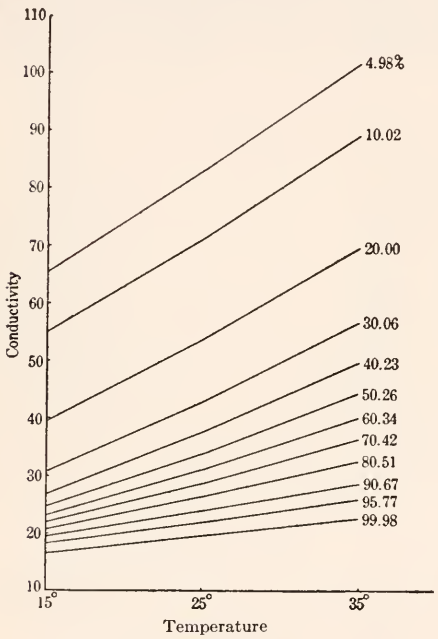


FIG. 39.—N/8 NaI.

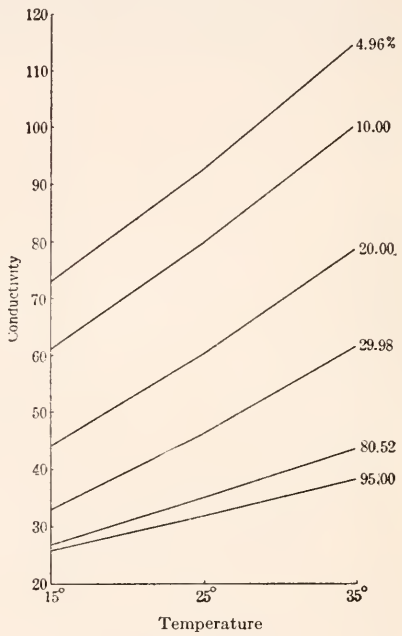


FIG. 40.—N/8 NaI.

The decrease in conductivity just mentioned is very rapid in the water end of the curve up to the 30 per cent alcohol, and from there on it is much more gradual. We may conclude from this, either that the first addition of alcohol to water has a much more marked effect on the association of the water than the addition of a little water to the alcohol has on the association of the alcohol, or that comparatively small quantities of alcohol increase the viscosity of water much more markedly than is the case when small quantities of water are added to alcohol; or, again, that there is a sudden change in the hydration of the dissolved substance caused by the addition of the alcohol, whereas water has a far smaller effect on the alcoholation; or, finally, that perhaps all or some of these factors combine to produce the effect. Let us analyze them.

[1]Amer. Chem. Journ., **34**, 377 and 384 (1905).

The third conclusion may be disposed of first as of little value, since it will be remembered that salts of the alkali metals are very little hydrated or alcoholated.

We have just seen, from a study of the viscosity data, that there is a marked negative viscosity, *i. e.*, positive fluidity, at the water end of the fluidity curves. On the other hand, there is a steadily increasing viscosity at the alcohol end. Moreover, the transition-point from positive to negative viscosity was shown to be nearer the pure water than the pure alcohol. To recapitulate, it was concluded from these

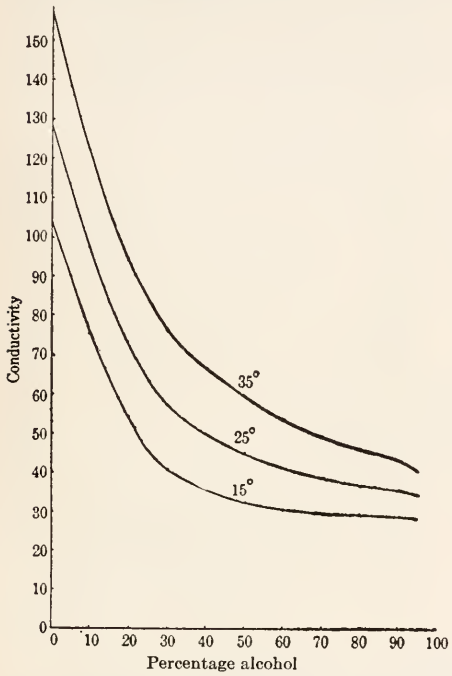


FIG. 41.—N/128 NaI.

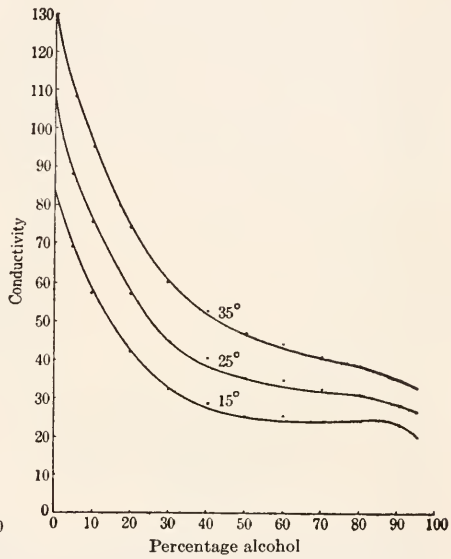


FIG. 42.—N/32 NaI.

results that the change in association brought about by the mixing of the two solvents appeared to take place more largely in the case of the water than of the alcohol.

Both our first and second conclusions, with regard to the phenomenon observed in the case of conductivity, appear, then, to be in perfect harmony with those concerning the association and the viscosity. As to the final conclusion, it obviously follows as a matter of course from what has preceded, since the association and viscosity are so closely related.

The decrease in the conductivity as a whole is more rapid for the potassium iodide than for the sodium iodide. This is what might have been expected from a study of the viscosity data, which, in turn, are affected by the relative ionic volumes of potassium and sodium. The former, having the larger volume, would have a greater negative effect

than the sodium on the solvent, this being the same in both cases. Although the ionic velocity of the potassium is the greater, this greater volume tends to slow it down more as the alcohol is approached.

There is an unusual downward deflection in the curves beyond the 80 per cent alcohol, increasing in steepness as the 100 per cent alcohol is approached, which at first puzzled us every much. The asymmetry, that is, the unsymmetrical appearance of our conductivity curves, had already been noted. Then the question arose, what would be the appearance of a symmetrical curve if the viscosity and conductivity at either end were symmetrical with respect to the 50 per cent mixture? What kind of a curve would we have? The answer to this question is given in figure 42, from which it can be seen, on comparison

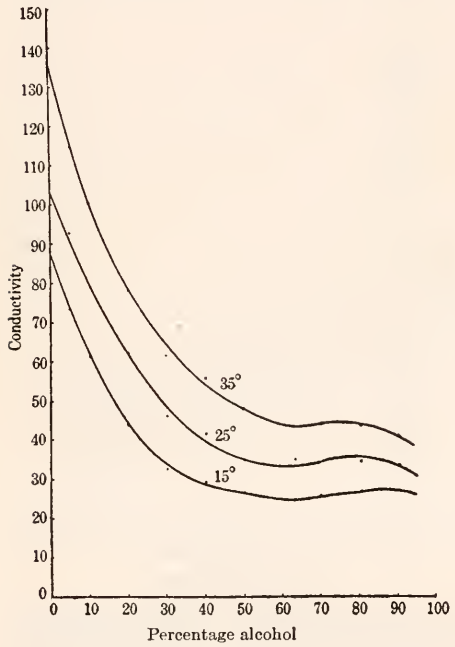


FIG. 43.—N/128 NaI.

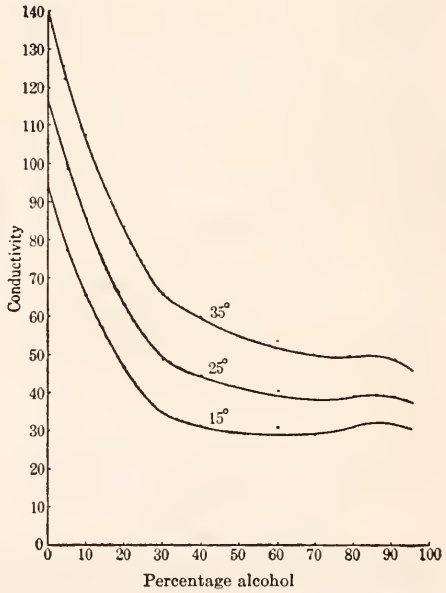


FIG. 44.—N/1024 NaI.

with the curves for the actual conductivity, that in the latter the point of symmetry has been shifted from the 50 per cent mixture to the 80 per cent, and that the end on the alcohol side is not really at the 100 per cent alcohol, but is imaginary, since the line at the 100 per cent point must be extended to make the curve symmetrical. To be more exact, we see here shifting similar to that noted above in the case of the transition-point in the fluidity; only, this happens at every temperature instead of with rise in temperature.

As the temperature rises the conductivity curves tend to become more and more nearly a linear function, that is, those for 35° have much less bend to them than those for 15°. A probable explanation

of this is that the fluidities of a series of such mixtures of alcohol and water tend also to become more nearly a linear function with rise in temperature.

In figure 39 we have plotted the conductivities of N/8 solution of sodium iodide in the various solvents with respect to temperature, making ordinates the conductivity and abscissas the temperatures. From this we observe that the temperature coefficients increase slightly with rise in temperature, with the exception of the 95 per cent mixture and the pure alcohol. Further, the increase becomes smaller as we approach the pure alcohol. The temperature coefficients themselves also become smaller as the percentage of alcohol becomes greater.

FIG. 45.

The slight increase in the temperature coefficients in the water end is doubtless due to the same cause which produces an increase in the temperature coefficients in pure water, namely, a breaking down of the hydrated ions with rise in temperature. As was said before, the salts of the alkali metal are only very slightly hydrated; therefore, the small increase in temperature coefficients.

Further, it is probable that since, with decrease in the amount of water, the increase in coefficients becomes less until there is none in the alcohol, the alcohol does not form alcoholates with these salts.

Thus far we have discussed only the relations which exist between the conductivities of the N/8 solutions. Reference to the curves for the other dilutions, figures 41, 42, 43, 44, and 45, will, however, show that the conclusions already arrived at also hold for them.

One point which should be noted is that in the case of sodium iodide there are distinct, though slight minima in the curves for N/128 and N/1024 solutions, occurring at about the 70 per cent alcohol. This phenomenon is not at all an unusual one, since practically everyone who has determined the conductivities of other substances in alcohol-water mixtures has found similar more or less pronounced minima. Almost all previous work was in dilute solutions.

SUMMARY.

It has been our endeavor throughout this investigation to improve the viscosity and conductivity methods wherever possible, in order to eliminate the grosser errors which ordinarily creep in, for example: temperature regulation; a more exact determination of the external resistance in the circuit; a change from suction to pressure as a means of raising the liquid in the viscosimeters, etc.

Instead of making up our solvents by the volume standard, as previous workers have done, we used the weight standard. An equation,

$$\frac{md'(p-x)}{xd} = y$$

was deduced and employed for determining the amounts by volume of the water necessary to add to 100 c.c., or even multiples of this quantity of alcohol, in order to make the required mixtures by weight.

Viscosity and conductivity determinations were made with several dilutions of potassium and sodium iodides, in a series of mixtures of alcohol and water; and curves representing fluidity as ordinates and percentages of alcohol as abscissas were drawn, as well as curves for conductivity as ordinates plotted both against mixtures of solvent and against temperatures as abscissas.

CONCLUSIONS.

We arrived at the following conclusions:

1. The effect of sodium and potassium iodides on the viscosity of ethyl alcohol-water mixtures is comparatively small for N/8 solutions.

2. There is a marked increase in the viscosity of the solvents caused by these salts in passing from the 100 per cent alcohol to the 60 per cent alcohol.

3. The shifting of the point at which the fluidity curve for the salt crosses that for the solvent with rise in temperature, is to be accounted for by the change in association of the solvent with rise in temperature.

4. This change in association is greater for the water than for the alcohol.

5. The facts brought out in connection with the viscosity work were in harmony with those discovered by previous workers, and therefore can be explained in the same way.

6. There is a continual decrease in the conductivity of N/8 sodium and potassium iodides in passing from pure water to pure alcohol. It is much more rapid in the large percentages of water than in the large percentages of alcohol.

7. This may be explained as due to the fact that the association of alcohol is changed to a much smaller extent by adding small quantities of water, than is water when to it small quantities of alcohol are added. Moreover, since association and viscosity are so closely related, we

also conclude that the same reasoning may be applied to the latter; in other words, there is a greater change in the viscosity of the water than of the alcohol.

8. The decrease in the conductivity of potassium iodide with the increase in the percentage of alcohol, is more rapid than the decrease for sodium iodide, due no doubt to the greater atomic volume of the former.

9. Hydration has practically no effect on the conductivity at any one temperature. With rise in temperature, however, the breaking down of the slightly hydrated ions causes a small increase in the temperature coefficients in most of the solutions containing water. In alcohol the temperature coefficients are a linear function, and therefore there is no alcoholation.

10. As the temperature rises the curves tend to become more and more nearly a linear function. We attribute this to the fact that as the temperature rises the fluidity curves also tend to become more nearly linear.

CHAPTER V.

CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF RUBIDIUM SALTS IN MIXTURES OF ACETONE AND WATER.

By P. B. Davis and H. Hughes.

The work done in the Chemical Laboratory of the Johns Hopkins University during the past dozen years, on the relations between the viscosities of solvents and solutions of certain salts in these solvents, was referred to at the beginning of the last chapter. That which is closely related to the contents of this chapter is the work of Jones and Veazey, Jones and Schmidt, Jones and Guy, and especially that of Jones and Davis.[1] The last named extended the work in glycerol as a solvent, studying especially the conductivities and viscosities of glycerol solutions of ammonium and rubidium salts, as has already been pointed out.

All previous work in the laboratory with acetone as a solvent shows that it has exceptional properties. Measurements of both conductivity and fluidity have usually given results that are abnormal in terms of other solvents; for this reason it was chosen as a solvent in this investigation, in the hope that the property possessed by rubidium salts of forming solutions having a lower viscosity than that of the solvent might throw some additional light upon the phenomena presented by solution. Only mixtures of acetone and water have been used, because in pure acetone the rubidium salts studied are not sufficiently soluble to affect the fluidity to a measurable extent.

EXPERIMENTAL.

CONDUCTIVITY APPARATUS.

Bridge.—The conductivity measurements were made by means of a slide-wire bridge about 5 meters long, the balance being detected by a telephone receiver. The bridge and rheostat were made and standardized by Leeds and Northrup Co., of Philadelphia, Pennsylvania; and the rheostat was compared with one recently standardized by the United States Bureau of Standards.

A double system of wiring was used between the rheostat, slide wire, and cells, so that by means of a double-arm double-throw switch the arms of the bridge could be interchanged. In this way the resistance a of the first portion of the slide wire was read and then $b = 1000 - a$ for comparison. The circuit was opened and closed by an ordinary telegraph key, whose resistance was made of negligible value by connecting the frame to the lever by a short spring of large copper wire.

The wire used throughout was number 12 gage, and the cells containing the solutions were connected with the rest of the bridge by a large flexible cable of copper having a negligible resistance. All connections were soldered, and the various portions of the apparatus were

[1]Carnegie Inst. Wash. Pubs. Nos. 80 and 180.

tested for any appreciable resistance. The two halves of the double system for reading a and b were carefully compared, and b was found not to differ from $1,000 - a$ by any appreciable quantity, except for resistances smaller than any used in this investigation—that is, below 10 ohms.

Cells.—The conductivity cells were of three forms. For the most concentrated solutions two U cells with adjustable electrodes were employed, having constants of about 15,000 and 30,000. The most dilute solutions and the solvents were measured in cells with cylindrical electrodes of the type described by Jones and Schmidt,[1] and by Jones and Kreider,[2] and with constants ranging from 2.9 to 4.3. The intermediate dilutions, that is, from N/10 to N/400 solutions, were measured in cells of the plate type described by Jones and Bingham.[3]

Constant-temperature Baths.—The constant-temperature baths used in both parts of this investigation were of the same general type employed for such work in this laboratory, and consisted essentially of round, galvanized-iron tubs of about 20 liters capacity, covered with non-conducting material. For the viscosity work the baths were equipped with large glass windows in the upper walls, 180° apart.

A more efficient form of stirrer provided with double journals and 6-bladed propellers was employed, and the brackets supporting these were attached directly to the walls of the building. The stirrers were driven by a round belt, at about 200 revolutions per minute, by a $\frac{1}{3}\frac{1}{2}$-horsepower water-cooled hot-air engine. These improvements lessened materially the vibrations due to side-thrust from the propellers, and increased the up-and-down stirring of the water in the bath, at the same time giving less circular motion.

By means of the pressure from a 2.5 meter stand-pipe, water could be kept flowing through special cooling coils of copper placed in the bottoms of the baths. This facilitated temperature regulation at or below room temperature. An auxiliary coil immersed in an ice-bath was also introduced into the cooling system by means of brass unions, whenever the average temperature of the tap-water approached too closely to the lowest temperature at which the work was attempted.

Temperature Regulation.—Temperature regulation of a high degree of accuracy was obtained by equipping all baths with an approved form of electrically operated gas-valve, consisting essentially of a sensitive 150-ohm relay, to the armature of which was attached a device for cutting down the flow of gas whenever the relay was set in action by the thermo-regulator in the bath. The relays were connected in parallel on a 2.5-volt circuit from accumulators, and were operated by an improved form of mercury thermo-regulator of the general type described by Morse, but having 2 to 4 reservoir tubes of special hydrometer tubing, with walls about 0.25 mm. thick. A maximum surface of mercury was thus secured, in keeping with the stability of the instrument. A more detailed description of the above forms is to be found

[1]Amer. Chem. Journ., **42**, 39 (1909). [2]*Ibid.*, **45**, 282 (1911). [3]*Ibid.*, **34**, 481 (1905)

in our work with Wightman on conductivity and viscosity in alcohol-water mixtures.[1]

With this improved form of apparatus we have maintained a constant temperature over any desired length of time to within 0.01°, for temperatures from 15° to 40°, and at 25° with moderate precautions variations in temperature not more than 0.005° resulted. An additional advantage of the type of thermo-regulators described above, over the more complicated toluol-mercury and other froms, lies in its simplicity and in the fact that it may be readily constructed by anyone possessing moderate skill in glass manipulation. The lengths of the reservoir tubes need be limited only by the depth of the baths used. In this work tubes 25 cm. long and 7 cm. interior diameter were found to be most satisfactory. The thermometers used were of the Beckman type graduated to 0.02°; and these were compared at frequent intervals with a thermometer which had been standardized within the year by the United States Bureau of Standards.

VISCOSITY APPARATUS.

The viscosity apparatus used throughout this investigation was the same essentially as that described in our work with glycerol.[2] Special precautions were taken to eliminate, as far as possible, several annoying sources of error. Vibrations of the instruments due to external causes were guarded against by making use of a special support for the viscosimeters, consisting of a heavy tripodal leveling base resting on several layers of thick piano felt, and a large bronze standard to which a horizontal arm was rigidly attached by a collar and set-screw. The viscosimeters were supported in the bath against a cork-covered brass plate at the extremity of this arm, by means of a spring clamp, the tension of which was adjusted to different instruments by a thumb-screw.

Further precautions were taken against vibrations by removing the engine and stirrer brackets from direct contact with the desk supporting the baths and viscosimeter stand.

It was necessary also to guard against dust particles, which would tend to clog the capillary of the viscosimeter. To this end special precautions were necessary, both in making up solutions and in using them in the viscosimeters. It was found necessary to use silk instead of linen in polishing all weighing vessels, and to wash out all flasks with dust-free water and alcohol, and then dry them by a blast of air filtered through cotton wool. The viscosimeters were thoroughly cleansed with chromic acid before each procedure, washed as above, and dried by aspirating hot, dust-free air through them. For this purpose the air was drawn through glass wool, over calcium chloride in a long drying-tower, then through cotton wool, and finally through a short iron tube heated in an asbestos chamber by means of a flat burner. A final filtration through cotton took place before the air

[1]Jour. Chim. Phys. (1913). Chapter IV, this monograph.
[2]Carnegie Inst. Wash. Pub. No. 180 (1913).

was drawn into the viscosimeter. The instruments were thus thoroughly and quickly dried, and examination with a hand-lens showed complete absence of dust particles in the capillary or bulb tubes.

When it was necessary to take a series of readings on a particular viscosimeter, this was equipped with a special head designed to exclude moisture and dust particles from contact with the liquid in the instrument. The liquid was then raised to the upper mark on the small bulb by means of a constant air-pressure apparatus, using the same stand-pipe as the cooling system. Air entering the viscosimeter from the pressure vessel was first carefully dried and freed from dust by the use of fused calcium chloride and cotton wool, and by means of stop-cocks all external air was excluded during the actual time of flow of the liquid through the capillary.

By observing the precautions noted above we have succeeded in obtaining from 3 to 5 consecutive readings on any particular viscosimeter, all agreeing to within the limits of error of the stop-watch used, which was a fine split-second Swiss instrument, reading to 0.2 second and adjusted with great accuracy. This watch had the additional advantage of running continuously, whether the hands were released or not, and gave much better results than the intermittent form heretofore used. Frequent comparisons were made with standard chronometers, and no errors of sufficient magnitude to affect the accuracy of the work were detected.

Specific-gravity determinations were made with a modified form of the Ostwald pycnometer, which is so well known that it does not require further description.

All flasks were carefully calibrated to hold aliquot parts of the true liter at 20°, and solutions were brought to within 0.1° of this temperature before being diluted to the mark.

SOLVENTS.

Water.—The water was purified by the method of Jones and Mackay[1] as modified by Schmidt, and has a mean specific conductivity of 1.5×10^{-6} at 25°.

Acetone.—Kahlbaum's so-called pure acetone was allowed to stand for several days over calcium chloride, and distilled two or three times. No difficulty was experienced in obtaining a product of approximately the same conductivity as the water used in this work. Solutions were made up as quickly as possible after distilling the acetone, which was always kept in a dark place.

Mixtures of Acetone and Water.—The mixtures used as solvents were made by diluting a given volume of acetone to a definite volume with water at 20°. For convenience, the number of cubic centimeters of acetone diluted to 100 c.c. was indicated as the "percentage" of acetone in the solvent. A very considerable contraction takes place when acetone and water are mixed, so that the figures used to designate the

[1]Amer. Chem. Journ., **17**, 83 (1895).

mixture are, of course, not true percentages either by weight or volume. The true percentage, however, is of no consequence so long as the mixture is thus defined. Actually, the mixture of 500 c.c. acetone diluted to 1 liter at 20° contains about 42 per cent by weight of acetone, and the mixture of 250 c.c. of acetone diluted to 1 liter contains approximately 20 per cent by weight of acetone.

SOLUTIONS.

Solutions of one-tenth normal and all greater concentrations were made by dissolving the requisite weight of salt. The N/50 and N/100 solutions were made from the N/10 by dilution; and the N/200 and N/400, respectively, were made from these. The N/800 and N/1600 concentrations were prepared in the same manner from the N/200 and N/400. The last two concentrations were thus made in three dilutions from the N/10 concentration. Upon the basis of a probable percentage deviation of 0.10 per cent in the original weight of salt, and in the measurement of the solvent in the flask, and of 0.40 per cent in the measurements from the burettes, the probable errors in the value of V at these greatest dilutions is about 0.70 per cent. The probable error in the other dilutions is, of course, much less than this, being within 0.14 per cent in the case of the N/10 and all greater concentrations.

All solutions were made up at 20°. No correction for changed normality at higher temperatures had been applied to the values obtained for molecular conductivity. Rise in temperature, of course, diminishes the normality of a solution. This effect is accompanied by an increase in molecular conductivity which is complex. While this increase in conductivity due to temperature, is of the same order of magnitude as that produced by the same lowering of normality caused by diluting with more of the solvent, the two effects bear no known relation to each other.

SALTS.

The rubidium salts used in this work were Kahlbaum's purest products. They were recrystallized two or three times from conductivity water, precipitated and washed with alcohol, and dried at 120° to 135° according to the nature of the salt. The iodide was pure white after drying, and the more concentrated solutions were only slightly colored after standing several days.

PROCEDURE.

CONDUCTIVITY MEASUREMENTS.

The values of the molecular conductivity μ_v are computed from the relation $\mu_v = K\frac{va}{wb}$, where v is the number of liters of solvent containing a gram-molecular weight of the salt; w, the resistance in ohms; a/b, the ratio from the Wheatstone bridge; and K, the cell constant.

The cell constants were determined with solutions of potassium chloride of N/50, N/500, and N/200 concentrations. The value taken

for the molecular conductivity of the N/50 solution was that given by Ostwald, namely, 129.7 reciprocal Siemens units at 25°. Three resistances were used in the measurement of each solution.

It should be pointed out that the fact that w is measured in ohms is not incongruous with the use of reciprocal Siemens units in the result, the factor 1/1.063 being included in the cell constants obtained. To convert the results given in the tables into reciprocal ohms, it is only necessary to multiply by 1.063.

The calculation of data was facilitated by the use of tables of values of $\frac{a}{b}\times\frac{1}{w}$. By use of notation by powers of 10, twenty values of $\frac{1}{w}$ were sufficient for the preparation of these tables, which were readily computed with a calculating machine. Not only does the use of such tables save considerable time in computation, but in their preparation the chances of mistakes are eliminated by methods which do not obtain when the values are independently computed. The tables used in this work gave all Wheatstone-bridge ratios from 400/600 to 600/400 to millimeters with interpolations to tenths of millimeters.

The greatest error in the measurements of the components K, v, a, b, of the molecular conductivity μ_v occurs in the determination of the cell constants of the plate cells. This is subject to considerable variation, and it was necessary to make frequent determinations of these values. Under average conditions the precision of μ_v is from 0.5 to 1.0 per cent.

Temperature Coefficients.—The temperature coefficient in conductivity units is the increase in conductivity for each degree rise in temperature; that is,

$$\text{Temp. coeff.} = \frac{\mu_{t2}-\mu_{t1}}{t_2-t_1}$$

the temperatures compared always differing from each other by 10°. The temperature coefficients in per cent is the above quantity divided by the conductivity at the lower temperature and multiplied by 100, *e. g.*,

$$\text{Percentage coefficient} = \frac{\mu_{35°}-\mu_{25°}}{10}\cdot\frac{100}{\mu_{25°}}$$

Viscosity measurements were calculated from the formula $\frac{\eta}{\eta_0} = \frac{st}{s_0t_0}$ in which η is the viscosity coefficient for the liquid in question, η_0 the absolute viscosity of water, s the specific gravity of the liquid at the given temperature, t the time of flow of the same, s_0 and t_0 the density and time of flow of water at the same temperature.

Fluidity was calculated from the formula $\phi = \frac{1}{\eta}$ where ϕ represents the fluidity.

TABLE 30.—*Molecular conductivities and temperature coefficients of rubidium salts in acetone-water mixtures at 15°, 25°, 35°, and 45°.*

RUBIDIUM CHLORIDE.

Mixture.	Molecular conductivities.					Temperature coefficients.					
						Conductivity units.			Per cent.		
	V	15°	25°	35°	45°	15 to 25°	25 to 35°	35 to 45°	15 to 25°	25 to 35°	35 to 45°
In 75 per cent acetone	4	25.5	30.4	35.5	40.9	0.490	0.502	0.548	1.92	1.65	1.55
	10	32.5	43.1	50.1	....	1.063	0.696	....	3.27	1.62	....
	200	50.8	63.1	76.0	88.0	1.229	1.30	1.20	2.42	2.06	1.58
In 62.5 per cent acetone	2	30.9	37.7	44.8	52.8	0.688	0.710	0.798	2.23	1.88	1.78
	10	39.0	47.9	57.2	66.7	0.891	0.922	0.955	2.28	1.93	1.67
	200	52.5	66.5	82.8	97.4	1.20	1.632	1.46	2.37	2.46	1.77
In 50 per cent acetone	2	39.1	48.8	59.0	69.8	0.975	1.020	1.077	2.49	2.09	1.82
	10	45.6	59.5	70.9	81.8	1.388	1.144	1.090	3.04	1.93	1.54
	200	56.7	72.5	90.3	108.6	1.58	1.78	1.83	2.79	2.45	2.03
In 37.5 per cent acetone	2	49.3	61.5	74.8	88.9	1.225	1.325	1.419	2.49	2.16	1.90
	10	54.5	69.2	84.4	101.5	1.473	1.526	1.708	2.71	2.21	2.03
	200	63.0	82.6	100.1	121.3	1.952	1.759	2.12	3.10	2.13	2.12
In 25 per cent acetone	2	59.0	73.9	89.3	106.0	1.495	1.541	1.668	2.54	2.08	1.87
	10	62.8	78.0	93.3	110.0	1.520	1.532	1.674	2.42	1.97	1.80
	200	73.6	94.1	116.1	140.0	2.041	2.201	2.39	2.77	2.34	2.06
In 12.5 per cent acetone	2	74.3	91.2	109.4	127.9	1.692	1.819	1.850	2.28	2.00	1.69
	200	90.5	115.1	138.4	164.9	2.46	2.33	2.65	2.72	2.02	1.91

RUBIDIUM BROMIDE.

In 75 per cent acetone	2	28.2	33.5	38.8	43.9	0.529	0.53	0.52	0.188	1.58	1.34
	4	32.5	39.1	45.7	52.6	0.655	0.66	0.68	2.02	1.69	1.49
	10	39.1	47.6	55.9	64.7	0.845	0.83	0.88	2.16	1.74	1.57
	50	48.7	59.6	71.0	82.8	1.09	1.14	1.18	2.25	1.91	1.66
	100	52.3	64.2	76.8	89.5	1.19	1.26	1.27	2.28	1.96	1.65
	200	55.1	68.1	81.6	95.1	1.30	1.35	1.35	2.36	1.98	1.66
	400	58.4	71.8	85.8	100.9	1.34	1.40	1.51	2.30	1.95	1.76
	800	61.2	75.7	90.8	106.7	1.45	1.51	1.59	2.37	1.99	1.76
	1600	65.9	81.3	97.8	114.9	1.54	1.65	1.71	2.34	2.03	1.75
In 62.5 per cent acetone	2	36.2	44.2	52.7	61.5	0.80	0.84	0.88	2.18	1.90	1.67
	10	43.5	53.9	63.8	74.2	1.04	0.99	1.04	2.39	1.84	1.63
	200	56.5	72.7	87.1	103.9	1.62	1.44	1.68	2.87	1.98	1.93
In 50 per cent acetone	1	40.9	50.5	60.6	71.3	0.956	1.01	1.07	2.34	2.01	1.76
	2	43.3	54.2	65.7	77.8	1.09	1.15	1.21	2.51	2.12	1.82
	4	45.8	57.9	70.6	84.7	1.21	1.27	1.41	2.64	2.19	2.00
	10	47.8	59.8	72.5	84.8	1.20	1.27	1.23	2.51	2.13	1.70
	50	54.6	69.8	86.3	103.0	1.52	1.65	1.67	2.78	2.37	1.94
	100	56.6	72.4	89.9	107.9	1.58	1.75	1.80	2.80	2.42	2.00
	200	57.5	73.8	91.5	110.0	1.63	1.77	1.85	2.84	2.40	2.02
	400	59.3	76.1	94.5	113.3	1.68	1.84	1.88	2.83	2.42	1.99
	800	60.7	78.1	97.4	117.2	1.74	1.93	1.98	2.87	2.47	2.03
	1600	61.6	79.2	98.5	118.4	1.76	1.93	1.99	2.86	2.44	2.02
In 37.5 per cent acetone	2	51.1	64.2	78.4	93.4	1.31	1.42	1.50	2.55	2.22	1.92
	10	54.3	67.7	82.2	96.5	1.35	1.55	1.43	2.48	2.28	1.74
	200	64.8	83.8	104.0	125.0	1.91	2.02	2.10	2.94	2.41	2.02
In 25 per cent acetone	2	61.2	76.6	92.6	109.7	....	....	....	....	....	.....
	10	63.7	79.2	95.4	111.6	....	....	....	....	....	.....
	50	73.3	93.8	115.4	138.4	....	....	....	....	....	.....
	200	75.7	96.9	119.7	143.6	....	....	....	....	....	.....
In 12.5 per cent acetone	2	75.6	93.1	111.5	130.3	....	....	....	....	....	.....
	10	81.7	102.3	123.5	146.0	....	....	....	....	....	.....

TABLE 30.—*Molecular conductivities and temperature coefficients of rubidium salts in acetone-water mixtures at 15°, 25°, 35°, and 45°*—Continued.

RUBIDIUM IODIDE..

Mixture.	Molecular conductivities.					Temperature coefficients.					
						Conductivity units.			Per cent.		
	V	15°	25°	35°	45°	15 to 25°	25 to 35°	35 to 45°	15 to 25°	25 to 35°	35 to 45°
In 75 per cent acetone.....	1	36.2	43.0	50.6	57.6	0.68	0.75	0.71	1.88	1.75	1.40
	4/3	37.1	44.1	52.0	59.8	0.70	0.69	0.78	1.89	1.56	1.50
	2	38.8	46.4	53.8	61.5	0.75	0.74	0.73	1.93	1.63	1.36
	4	42.7	51.3	59.7	68.5	0.87	0.84	0.88	2.03	1.67	1.47
	10	....	58.0	68.2	78.7	....	0.93	1.05	....	1.61	1.53
	50	....	67.9	80.8	93.7	....	1.30	1.29	....	1.92	1.60
	100	58.7	71.8	85.7	99.5	1.38	1.39	1.38	2.37	1.93	1.61
	200	60.4	74.3	87.6	102.8	1.39	1.33	1.52	2.31	1.79	1.78
	400	62.5	76.3	91.2	107.3	1.38	1.49	1.61	2.21	1.95	1.77
	800	64.2	78.5	94.1	119.6	1.43	1.55	1.55	2.23	1.95	1.67
	1600	65.2	80.1	95.3	111.4	1.49	1.52	1.61	2.29	1.90	1.69
In 62.5 per cent acetone.....	2	42.8	53.0	63.3	74.2	1.01	1.13	1.09	2.37	2.13	1.73
	10	48.6	60.7	73.3	86.7	1.23	1.26	1.34	2.52	2.08	1.82
	200	57.5	72.7	89.1	106.5	1.52	1.65	1.74	2.64	2.27	1.95
In 50 per cent acetone.....	1	46.5	57.4	68.6	81.0	1.087	1.124	1.236	2.34	1.96	1.80
	4/3	46.7	58.1	69.8	82.9	0.940	1.169	1.314	2.02	2.01	1.89
	2	47.2	58.8	71.0	83.9	1.16	1.22	1.29	2.45	2.08	1.82
	4	49.0	62.0	76.0	91.8	1.301	1.40	1.575	2.68	2.26	2.07
	10	51.5	65.3	80.3	95.2	1.379	1.502	1.49	2.68	2.33	1.86
	50	55.5	71.0	87.7	105.7	1.55	1.67	1.80	2.79	2.35	2.05
	100	56.6	72.2	89.7	108.8	1.56	1.75	1.91	2.76	2.42	2.13
	200	58.3	74.9	92.8	112.3	1.56	1.79	1.95	2.68	2.39	2.10
	400	59.0	75.8	94.0	114.1	1.68	1.82	2.01	2.85	2.40	2.14
	800	60.2	77.7	95.9	116.5	1.75	1.82	2.06	2.91	2.35	2.15
	1600	62.5	78.8	96.9	120.5	1.63	1.81	2.36	2.61	2.30	2.28
In 37.5 per cent acetone.....	2	53.8	67.9	82.8	98.7	1.41	1.49	1.59	2.62	2.19	1.92
	10	56.2	72.7	89.4	107.1	1.66	1.66	1.77	2.95	2.28	1.99
	200	63.8	82.0	101.7	123.1	1.82	1.97	2.13	2.86	2.41	2.09
In 25 per cent acetone.....	1	62.7	77.3	92.5	108.5	1.45	1.52	1.61	2.32	1.97	1.74
	4/3	63.0	77.9	94.1	110.6	1.49	1.62	1.65	2.36	2.09	1.75
	2	63.9	78.9	95.7	113.8	1.59	1.68	1.81	2.52	2.12	1.89
	4	63.0	80.4	98.7	117.3	1.65	1.84	1.85	2.58	2.28	1.88
	10	65.1	83.2	101.8	121.6	1.81	1.86	1.98	2.78	2.24	1.94
	50	70.8	90.2	111.0	133.4	1.94	2.08	2.24	2.74	2.31	2.01
	100	72.0	91.7	113.1	135.9	1.97	2.14	2.28	2.74	2.34	2.02
	200	74.2	94.5	117.1	139.9	2.03	2.26	2.28	2.74	2.39	1.95
	400	74.0	94.1	116.8	140.1	2.01	2.27	2.33	2.72	2.42	2.00
	800	75.1	95.6	118.5	145.2	2.05	2.29	2.67	2.73	2.40	2.25
	1600	75.8	96.4	118.3	141.5	2.06	2.19	2.32	2.72	2.28	1.96
In 12.5 per cent acetone.....	2	76.2	94.2	112.5	131.6	1.79	1.83	1.92	2.35	1.94	1.71
	10	80.6	100.4	121.4	144.0	1.98	2.09	2.26	2.43	2.01	1.86
	200	89.9	113.4	137.7	163.1	2.35	2.43	2.54	2.62	2.14	1.84

TABLE 30.—*Molecular conductivities and temperature coefficients of rubidium salts in acetone-water mixtures at 15°, 25°, 35°, and 45°*—Continued.

RUBIDIUM NITRATE.

Mixture.	Molecular conductivities.					Temperature coefficients.					
						Conductivity units.			Per cent.		
	V	15°	25°	35°	45°	15 to 25°	25 to 35°	35 to 45°	15 to 25°	25 to 35°	35 to 45°
In 75 per cent acetone	4	32.8	39.4	46.4	53.7	0.658	0.694	0.74	2.01	1.77	1.60
	10	40.0	48.3	56.9	65.7	0.827	0.86	0.88	2.07	1.78	1.55
	50	51.3	62.5	74.1	86.2	1.12	1.16	1.21	2.19	1.96	1.64
	100	55.4	67.4	80.7	93.9	1.20	1.33	1.32	2.17	1.98	1.64
	200	58.8	71.6	85.3	99.5	1.28	1.37	1.42	2.18	1.92	1.67
	400	61.1	74.4	89.0	104.3	1.33	1.46	1.53	2.18	1.96	1.72
	800	63.7	79.0	94.2	110.6	1.43	1.52	1.64	2.21	1.93	1.74
	1600	67.5	82.2	98.1	115.3	1.47	1.59	1.72	2.18	1.94	1.75
In 62.5 per cent acetone	4	38.8	48.0	57.8	68.1	0.926	0.98	1.03	2.39	2.04	1.78
	10	44.3	55.2	66.4	78.2	1.09	1.13	1.18	2.47	2.05	1.77
	200	57.1	71.9	87.0	103.8	1.48	1.51	1.68	2.59	2.09	1.93
In 50 per cent acetone	2	39.9	50.2	60.9	72.4	1.03	1.07	1.15	2.59	2.13	1.89
	4	43.7	55.2	67.3	80.7	1.16	1.21	1.34	2.65	2.19	1.99
	10	48.2	61.5	74.8	89.3	1.33	1.33	1.45	2.76	2.16	1.94
	50	54.8	69.8	85.8	103.1	1.50	1.60	1.73	2.74	2.29	2.02
	100	56.7	72.4	89.1	107.3	1.57	1.67	1.82	2.77	2.31	2.04
	200	58.0	75.6	91.9	110.2	1.76	1.63	1.83	3.02	2.16	1.99
	400	59.3	75.5	93.1	112.3	1.62	1.76	1.92	2.73	2.33	2.06
	800	60.2	77.1	95.0	115.3	1.69	1.79	2.03	2.81	2.33	2.14
	1600	59.2	76.2	94.0	113.9	1.70	1.78	1.99	2.88	2.34	2.12
In 37.5 per cent acetone	2	45.7	57.6	70.5	84.7	1.19	1.29	1.42	2.61	2.24	2.00
	10	54.4	69.4	84.7	101.4	1.49	1.53	1.67	2.75	2.21	1.98
	200	63.9	81.7	101.2	122.0	1.78	1.95	2.08	2.78	2.39	2.05
In 25 per cent acetone	2	54.4	68.3	82.9	98.2	1.40	1.45	1.53	2.57	2.13	1.85
	4	58.2	73.5	89.6	106.9	1.43	1.61	1.73	2.47	2.19	1.93
	10	61.0	75.1	91.5	110.3	1.41	1.64	1.88	2.31	2.19	2.06
	50	69.2	87.8	107.7	128.8	1.86	1.99	2.11	2.69	2.27	1.96
	100	71.2	90.6	111.4	133.5	1.94	2.08	2.21	2.78	2.30	1.98
	200	73.3	93.5	114.9	137.5	2.02	2.12	2.28	2.76	2.27	1.99
	400	73.0	92.9	114.9	137.6	1.99	2.20	2.27	2.73	2.34	1.98
	800	79.4	100.4	123.6	147.7	2.10	2.32	2.41	2.65	2.31	1.95
	1600	73.3	92.8	114.2	136.6	1.95	2.14	2.24	2.66	2.31	1.96
In 12.5 per cent acetone	2	65.1	80.6	96.8	113.7	1.55	1.62	1.69	2.38	2.00	1.75
	10	74.1	91.7	106.9	123.9	1.76	1.51	1.71	2.37	1.65	1.60
	200	87.0	108.8	131.7	156.4	2.18	2.29	2.47	2.50	2.10	1.88

TABLE 31.—*Viscosity, fluidity, and temperature coefficients of fluidity of rubidium salts in mixtures of acetone with water.*

RUBIDIUM CHLORIDE.

Mixture.	Mol. conc.	η 15°	η 25°	η 35°	η 45°	ϕ 15°	ϕ 25°	ϕ 35°	ϕ 45°	Temperature coefficients.		
										15 to 25°	25 to 35°	35 to 45°
In 75 per cent acetone with water...	0.50	See note	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	0.25	0.01157	0.00927	0.00756	0.00628	86.38	107.9	137.2	159.2	0.0249	0.0234	0.0204
	0.10	0.01137	0.00910	0.00742	0.00615	87.95	109.9	134.7	162.6	0.0249	0.0226	0.0207
	Solv.	0.01116	0.00891	0.00725	0.00602	89.61	112.2	137.9	166.0	0.0252	0.0229	0.0204
In 62.5 per cent acetone with water..	0.50	0.01568	0.01212	0.00967	0.00794	63.78	82.50	103.4	125.9	0.0293	0.0253	0.0218
	0.10	0.01526	0.01174	0.00916	0.00745	65.50	85.17	109.2	134.2	0.0300	0.0282	0.0229
	Solv.	0.01514	0.01177	0.00912	0.00738	66.05	85.96	109.6	135.5	0.0286	0.0289	0.0236
In 50 per cent acetone with water...	0.50	0.01744	0.01336	0.01037	0.00832	56.36	74.85	96.43	120.3	0.0328	0.0288	0 0248
	0.10	0.01778	0.01322	0.01030	0.00818	56.24	75.65	97.13	122.2	0.0345	0.0284	0.0258
	Solv.	0.01774	0.01729	0.01026	0.00818	56.37	75.14	96.49	122.2	0.0333	0.0284	0.0266
In 37.5 per cent acetone with water..	0.50	0.01933	0.01376	0.01071	0.00857	51.74	72.69	93.34	116.7	0.0405	0.0289	0.0251
	0.10	0.01820	0.01354	0.01044	0.00829	54.93	73.83	95.78	120.6	0.0344	0.0297	0.0259
	Solv.	0.01825	0.01364	0.01036	0.00825	54.80	73.31	96.42	121.2	0.0338	0.0315	0.0257

TABLE 31.—*Viscosity, fluidity, and temperature coefficients of fluidity of rubidium salts in mixtures of acetone with water*—Continued.

RUBIDIUM BROMIDE.

Mixture.	Mol. conc.	η 15°	η 25°	η 35°	η 45°	ϕ 15°	ϕ 25°	ϕ 35°	ϕ 45°	Temperature coefficients.		
										15 to 25°	25 to 35°	35 to 45°
In 75 per cent acetone with water...	0.50	0.01204	0.00963	0.00794	0.00667	83.07	103.9	126.0	149.9	0.0251	0.0212	0.0189
	0.25	0.01162	0.00925	0.00758	0.00639	86.06	108.1	131.6	156.5	0.0256	0.0220	0.0187
	Solv.	0.01114	0.00886	0.00721	0.00599	89.76	112.8	138.6	166.9	0.0257	0.0229	0.0201
In 62.5 per cent acetone with water..	0.50	0.01556	0.01200	0.00951	0.00774	64.26	83.31	105.2	129.2	0.0296	0.0263	0.0228
	0.10	0.01547	0.01186	0.00936	0.00757	64.64	84.29	106.8	132.1	0.0304	0.0267	0.0237
	Solv.	0.01516	0.01158	0.00910	0.00731	65.99	86.37	109.9	136.8	0.0309	0.0272	0.0245
In 50 per cent acetone with water...	1.00	0.01772	0.01347	0.01060	0.00859	56.44	74.26	94.30	116.4	0.0316	0.0270	0.0234
	0.75	0.01781	0.01358	0.01119	0.00861	56.15	73.63	89.40	116.2	0.0311	.....	.....
	0.50	0.01778	0.01358	0.01061	0.00853	56.25	73.91	94.24	117.2	0.0314	0.0275	0.0244
	0.25	0.01774	0.01331	0.01038	0.00845	56.38	75.16	96.30	118.3	0.0333	0.0281	0.0229
	0.10	0.01774	0.01331	0.01039	0.00819	56.37	75.14	96.27	122.1	0.0333	0.0281	0.0268
	Solv.	0.01774	0.01329	0.01026	0.00818	56.37	75.14	96.49	122.2	0.0315	0.0284	0.0262
In 37.5 per cent acetone with water..	0.50	0.01780	0.01331	0.01028	0.00818	56.19	75.13	97.24	122.2	.....	.....	.....
	0.10	0.01823	0.01354	0.01038	0.00823	54.86	75.87	96.34	121.5	.....	.....	.....
	Solv.	0.01829	0.01361	0.01050	0.00827	54.69	73.46	95.43	120.9	.....	.....	.....
In 25 per cent acetone with water...	0.50	0.01630	0.01247	0.00978	0.00780	61.33	80.17	102.3	126.6	0.0337	0.0294	0.0257
	0.25	0.01642	0.01228	0.00954	0.00767	60.89	81.49	104.9	130.3	.....	.....	.....
	0.10	0.01658	0.01227	0.00950	0.00757	60.31	81.52	105.2	132.2	0.0347	0.0304	0.0261
	Solv.	0.01699	0.01266	0.00975	0.00779	59.05	79.01	102.6	128.3	0.0343	0.0297	0.0267
In 12.5 per cent acetone with water..	0.05	0.01367	0.01065	0.00847	0.00695	73.14	93.87	118.1	143.9	0.0307	0.0276	0.0238
	0.10	0.01415	0.01086	0.00852	0.00698	70.65	92.09	117.4	143.3	0.0330	0.0291	0.0256
	Solv.	0.01430	0.01086	0.00855	0.00698	69.91	92.05	116.9	143.4	0.0338	0.0299	0.0250

TABLE 31.—*Viscosity, fluidity, and temperature coefficients of fluidity of rubidium salts in mixtures of acetone with water*—Continued.

RUBIDIUM IODIDE.

Mixture.	Mol. conc.	η 15°	η 25°	η 35°	η 45°	ϕ15°	ϕ25°	ϕ35°	ϕ45°	Temperature coefficients.		
										15 to 25°	25 to 35°	35 to 45°
In 75 per cent acetone with water...	1.00	0.01338	0.01087	0.00912	0.00751	74.74	91.97	109.7	132.2	0.0231	0.0192	0.0214
	0.75	0.01276	0.01027	0.00918	0.00702	78.36	97.38	122.3	142.4	0.0243	0.0256	0.0164
	0.50	0.01219	0.00974	0.00796	0.00664	82.06	102.7	125.7	150.7	0.0251	0.0224	0.0199
	0.25	0.01169	0.00936	0.00761	0.00633	85.51	106.9	131.3	158.0	0.0250	0.0228	0.0203
	0.10	0.01147	0.00918	0.00747	0.00620	87.20	108.9	133.9	161.3	0.0249	0.0229	0.0205
	Solv.	0.01119	0.00896	0.00728	0.00605	89.37	111.6	137.3	165.4	0.0248	0.0222	0.0205
In 62.5 per cent acetone with water..	0.10	0.01554	0.01195	0.00948	0.00774	64.34	83.72	105.5	129.1	0.0301	0.0287	0.0224
	0.50	0.01541	0.01182	0.00932	0.00758	64.91	84.60	107.3	131.9	0.0303	0.0268	0.0229
	Solv.	0.01509	0.01177	0.00914	0.00743	66.28	84.94	109.4	134.7	0.0282	0.0258	0.0231
In 50 per cent acetone with water...	1.00	0.02007	0.01623	0.01172	0.00938	49.82	61.62	85.32	106.6	0.0237	0.0385	0.0250
	0.75	0.01822	0.01362	0.01053	0.00842	54.89	73.40	94.96	118.7	0.0337	0.0294	0.0250
	0.50	0.01717	0.01334	0.01023	0.00824	58.29	74.96	97.74	121.3	0.0286	0.0304	0.0241
	0.25	0.01554	0.01178	0.00930	0.00749	64.36	84.90	107.5	133.5	0.0318	0.0266	0.0242
	0.10	0.01491	0.01149	0.00909	0.00743	67.06	87.01	110.0	134.5	0.0298	0.0264	0.0223
	Solv.	0.01779	0.01332	0.01029	0.00820	56.21	75.06	97.29	122.0	0.0353	0.0296	0.0254
In 37.5 per cent acetone with water..	0.50	0.01711	0.01044	0.01017	0.00810	58.44	95.78	98.29	123.5	.....	.....	0.0256
	0.10	0.01819	0.01356	0.01046	0.00930	54.96	73.76	95.56	120.5	0.0342	0.0296	0.0261
	Solv.	0.01836	0.01365	0.01037	0.00922	54.46	73.27	96.43	121.7	0.0345	0.0316	0.0262
In 25 per cent acetone with water...	1.00	0.01500	0.01156	0.00925	0.00761	66.66	86.48	108.2	131.4	0.0297	0.0251	0.0214
	0.75	0.01553	0.01196	(0.00952)	(0.00839)	64.39	83.65	.....	.....	0.0299	.....	.....
	0.50	0.01597	0.01314	0.00937	0.00970	62.60	82.35	.....	.....	0.0315	.....	.....
	0.25	0.01626	0.01218	0.00951	0.00767	61.50	82.10	105.2	130.3	0.0335	0.0281	0.0239
	0.10	0.01677	0.01261	0.00977	0.00787	58.62	79.28	102.3	127.1	0.0352	0.0291	0.0242
	Solv.	0.01714	0.01275	0.00883	0.00788	58.33	78.42	101.7	126.9	0.0345	0.0297	0.0247
In 12.5 per cent acetone with water..	0.50	0.01334	0.01034	0.00829	0.00678	74.95	96.70	120.6	147.4	0.0290	0.0247	0.0222
	0.10	0.01415	0.01085	0.00854	0.00697	70.68	92.20	117.0	143.5	0.0304	0.0269	0.0226
	Solv.	0.01442	0.01098	0.00862	0.00700	69.37	91.83	116.1	142.9	0.0323	0.0264	0.0231

TABLE 31.—*Viscosity, fluidity, and temperature coefficients of fluidity of rubidium salts in mixtures of acetone with water*—Continued.

RUBIDIUM NITRATE.

Mixture.	Mol. conc.	η 15°	η 25°	η 35°	η 45°	ϕ 15°	ϕ 25°	ϕ 35°	ϕ 45°	Temperature coefficients		
										15 to 25°	25 to 35°	35 to 45°
In 75 per cent acetone with water...	0.25	0.01155	0.00920	0.00753	0.00625	86.54	108.6	132.8	159.9	0.0255	0.0224	0.0204
	0.10	0.01136	0.00910	0.00741	0.00617	88.01	109.8	135.0	162.1	0.0248	0.0230	0.0201
	Solv.	0.01132	0.00889	0.00725	0.00602	89.83	112.4	137.8	166.2	0.0252	0.0226	0.0206
In 62.5 per cent acetone with water..	0.50	0.01562	0.01216	0.00962	0.00787	64.04	82.24	103.9	127.0	0.0284	0.0264	0.0222
	0.25	0.01496	0.01163	0.00920	0.00742	66.83	86.01	108.7	134.8	0.0287	0.0264	0.0240
	0.10	.....	0.01159	0.00909	0.00737	.....	86.29	110.0	135.6	.....	0.0274	0.0233
	Solv.	0.01516	0.01195	0.00914	0.00740	65.97	83.66	109.4	135.0	0.0268	0.0307	0.0234
In 50 per cent acetone with water...	0.50	0.01820	0.01373	0.01068	0.00858	54.94	77.83	93.63	116.6	0.0326	0.0286	0.0246
	0.25	(0.01714)	0.01301	0.01018	0.00824	.....	.....	98.23	121.4	.....	.....	0.0236
	0.10	0.01761	0.01308	0.01007	0.00801	56.79	76.45	99.30	124.8	0.0346	0.0299	0.0257
	Solv.	0.01769	0.01325	0.01022	0.00815	56.53	75.47	97.85	122.7	0.0335	0.0297	0.0253
In 37.5 per cent acetone with water..	0.50	0.01781	0.01344	0.01049	0.00845	56.15	74.42	95.32	118.3	0.0325	0.0281	0.0241
	0.10	0.01814	0.01349	0.01042	0.00830	55.11	74.15	95.97	120.5	0.0345	0.0294	0.0255
	Solv.	0.01810	0.01359	0.01021	0.00830	55.25	72.02	97.96	125.0	0.0304	0.0360	0.0275
In 25 per cent acetone with water...	0.50	0.01602	0.01224	0.00959	0.00777	62.42	81.70	104.3	128.7	0.0309	0.0277	0.0234
	0.25	0.01661	0.01252	0.00977	0.00781	60.21	79.87	102.4	128.0	0.0326	0.0282	0.0241
	Solv.	0.01696	0.01268	0.00981	0.00782	58.96	79.86	101.9	127.9	0.0337	0.0292	0.0255
In 12.5 per cent acetone with water..	0.50	0.01364	0.01060	0.00847	0.00695	71.76	94.31	118.0	140.9	0.0314	0.0251	0.0194
	0.10	0.01398	0.01080	0.00849	0.00689	70.42	92.66	117.8	145.1	0.0315	0.0271	0.0232
	Solv.	0.01420	0.01079	0.00844	0.00689	70.42	92.66	126.3	145.0	0.0315	.....	.....

TABLE 32.—*Comparison of the viscosity and fluidity values for rubidium bromide in acetone-water mixtures.*

Temp.	V	75 per cent.		62.5 per cent.		50 per cent.		37.5 per cent.	
		η	ϕ	η	ϕ	η	ϕ	η	ϕ
15°	2	0.01204	83.07	0.01556	64.26	0.01778	56.25	0.01780	56.19
	10	.....	.....	.01547	64.64	.01774	56.37	.01823	54.86
	Solv.	.01115	89.76	.01516	65.99	.01774	56.37	.01829	54.69
25°	2	.00963	103.9	.01200	83.31	.01353	73.91	.01331	75.13
	10	.....	.....	.01186	84.29	.01331	75.14	.01354	73.87
	Solv.	.00886	112.8	.01158	86.37	.01329	75.14	.01361	73.46
35°	2	.00794	125.0	.00951	105.2	.01061	94.25	.01028	97.24
	10	.....	.....	.00936	106.8	.01039	96.26	.01038	96.34
	Solv.	.00721	138.6	.00910	109.9	.01026	96.49	.01050	95.93
45°	2	.00667	149.9	.00774	129.2	.00853	117.2	.00818	122.2
	10	.....	.....	.00757	132.1	.00819	122.1	.00823	121.5
	Solv.	.00599	166.9	.00731	136.8	.00818	122.2	.00827	120.9

Temp.	V	25 per cent.		12.5 per cent.		0 per cent.	
		η	ϕ	η	ϕ	η	ϕ
15°	2	0.01630	61.33	0.01367	73.14	.....	.....
	10	.01658	60.31	.01415	70.65	.....	.....
	Solv.	.....	59.05	.01430	69.91	.....	.....
25°	2	.01247	80.17	.01005	93.87	0.00872	114.7
	10	.01227	81.52	.01086	92.09	.00880	113.6
	Solv.	.01266	79.01	.01086	92.05	.00891	112.2
35°	2	.00978	102.3	.00847	118.1	.00718	139.4
	10	.00950	105.2	.00852	117.4	.00717	139.4
	Solv.	.00975	102.6	.00855	116.9	.00720	138.9
45°	2	.00790	126.6	.00695	143.9	.00608	164.3
	10	.00756	132.1	.00698	143.3	.00596	167.7
	Solv.	.00779	128.3	.00698	143.3	.00597	167.5

DISCUSSION.

A parallel investigation of the viscosities and fluidities of solutions of the several salts studied has been carried on in connection with the conductivity side of the problem.

We have measured the viscosities of the tenth and half normal solutions of rubidium chloride, bromide, iodide, and nitrate, in all the various mixtures of acetone and water used as solvents; also the viscosities of the quarter, three-quarters, and whenever possible the normal solutions of the same salts in the mixtures designated as 75 per cent, 50 per cent, and 25 per cent acetone with water. It was not possible to obtain data on solutions of these salts in pure acetone, on account

of their difficult solubility in this solvent. However, their great solubility in water made it possible to obtain quite concentrated solutions in the majority of the mixed solvents, even in that containing 90 per cent acetone. Only in one instance, that of N/2 rubidium chloride in 75 per cent acetone, was a solution obtained which was non-miscible with the solvent at 20°, and at 15° a homogeneous solution was obtained. Table 31 contains the values found.

From our previous work on these salts in glycerol and water, we should naturally expect to find instances of negative viscosity in acetone-water mixtures. However, the peculiarity of acetone as a solvent at once makes itself evident. Except in those mixtures containing the larger percentage of water, it will be noted that these salts increase the viscosity of the various solvents. Jones and Veazey had already noted this phenomenon in the case of potassium sulphocyanate, but the negative effect produced by rubidium salts is so great in other solvents that the two classes of salts can hardly be regarded as comparable.

A glance at the tables will show that rubidium iodide and nitrate, the two salts found to give the greatest viscosity lowering in glycerol-water and their mixtures, produce a marked increase at all dilutions in the viscosity of the solvents up to the 50 per cent acetone mixture. Beyond this point the fluidity curve (fig. 46) for the salts crosses that of the solvent, and a negative viscosity effect becomes apparent in the mixtures containing the lower percentages of acetone. The 50 per cent mixture is apparently very close to the transition-point, since certain dilutions apparently increase the viscosity of the solvent, while others lower it. It would seem that in mixtures from 100 per cent to 50 per cent acetone the molecular volume of the dissolved salt is smaller than the molecular aggregates of the solvents; and in the other mixtures, larger. The salts lower the viscosity of pure water, because according to Jones and Veazey's theory their molecular volumes are greater than the complexes of the solvent. On the addition of acetone having apparently much larger molecular complexes, this negative viscosity effect becomes less and less with increasing percentage of acetone, until we reach a mixture in which the two factors balance one another. This point is in the neighborhood of the 50 per cent mixture. By still further increasing the percentage of acetone, the aggregates of the solvent exceed the molecules and ions of the solute in size and a positive viscosity effect results.

Associated with each table of viscosities and fluidities is a corresponding table of temperature coefficients. Their relations to those of conductivity are taken up in the discussion of that phase of the work, which immediately follows.

It was found by Jones and Veazey[1] that the curves expressing the fluidity of varying mixtures of acetone and water are almost exactly

[1]Amer. Chem. Journ., **37**, 405 (1907).

parallel to those for the conductivity of potassium sulphocyanate in solution in the same mixtures. The fluidity curve for acetone has a minimum between 37.5 per cent and 50 per cent; and the fluidity for the rubidium halides and nitrate has its minimum in approximately the same position (fig. 46). The conductivity curves, however, of the rubidium salts have their minima corresponding to a much greater percentage of acetone (fig. 47). As has been shown by previous workers, this minimum in fluidity occurs at the position where the breaking down of association of one solvent by the other is greatest. The conductivity depends upon the velocities of the ions and the degree of dissociation. The dissociation is least when the association of the solvent is least, and the speed of the ions is least when the fluidity is greatest. Therefore, if these were the only determining factors, the conductivity minima always correspond to the fluidity minima.

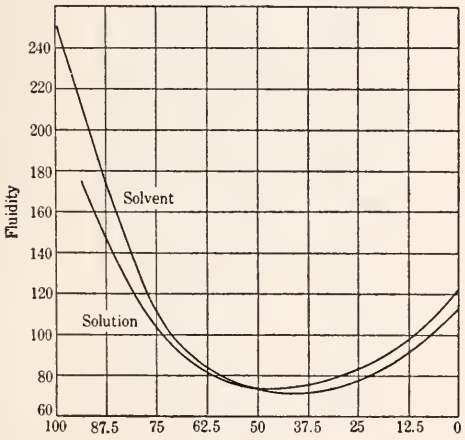


FIG. 46.—Fluidity of rubidium bromide, solution and solvent.

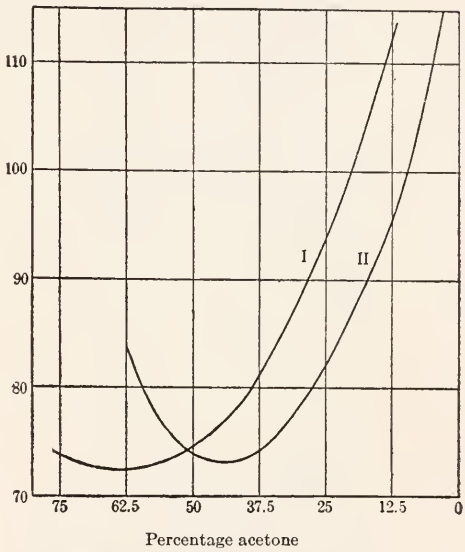


FIG. 47.—Conductivity and viscosity of rubidium iodide in acetone-water at 25°.
Curve I, ordinates, molecular conductivity.
Curve II, ordinates, fluidity.

Potassium sulphocyanate has a considerable solubility in pure acetone (about 20 grams in 100 grams of acetone at 20°), whereas the rubidium salts studied are only slightly soluble in pure acetone. Therefore, in the same concentrations, the rubidium salts are nearer saturation than potassium sulphocyanate. The percentage dissociation is, therefore, lower in the case of rubidium salts than in that of potassium sulphocyanate. A possible explanation of the shifting of the minimum in the conductivity of rubidium salts towards the greater proportions of acetone, is that the great insolubility in acetone might cause the disso-

ciation to be driven back. This shifting of the minimum by the slight solubility, however, seems to be clearly manifested only between salts with great difference in solubility in acetone, as is the case with potassium sulphocyanate and the rubidium halides. Of the four salts, rubidium chloride, iodide, bromide, and nitrate, the solubility in acetone of only the iodide is accurately known, so that these salts could not be compared with each other for the relation between solubility and minimum conductivity.

The relative solubilities in water probably do not correspond to the relative solubilities in acetone. The iodide and the nitrate are respectively the most soluble and the least soluble in water; but the conductivity minima of these two salts are the farthest from the ordinate, corresponding to 100 per cent acetone (figs. 48 to 51).

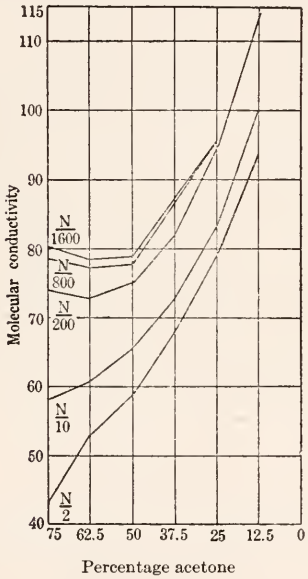


FIG. 48.—Conductivity of rubidium iodide in acetone-water at 25°.

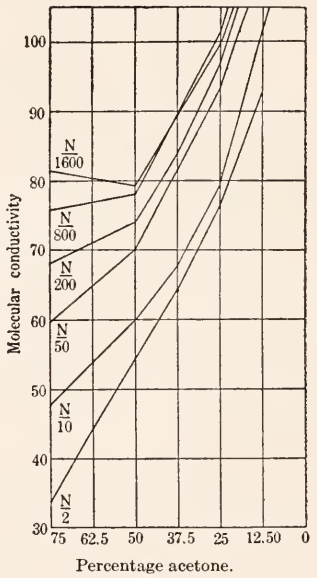


FIG. 49.—Conductivity of rubidium bromide in acetone-water at 25°.

It is not to be expected that the differences in solubility in water of the different rubidium salts would show this relation, because in the dilutions which are sufficiently great to give any minimum at all, these salts are very far from their saturation in water. In the dilutions greater than N/800, that is, where the dissociation approaches completeness, the minima in the conductivity curves are seen to be nearer those of fluidity (figs. 48 and 51).

A comparison of the percentage coefficients of fluidity given in tables 34 to 38 with those of conductivity, shows that the two are nearly equal, which is to be expected in the case of a non-solvated salt.

For the same salt the coefficients of conductivity, while nearly equal, are somewhat smaller than those of fluidity. As Davis and Jones have pointed out, this is due to "the decrease in association of the solvent with rise in temperature, causing a decrease in the ionization of the solute, and therefore a smaller conductivity."

In most cases the molecular conductivities of N/800 and N/1600 are practically the same, showing that the dissociation has apparently become nearly constant. If the conductivity depends only upon the velocity of the ions and the number of ions present, then, in the case of a non-hydrated electrolyte, since velocity is proportional to fluidity,

$$\frac{\mu_\infty \text{ in solvent}}{\mu_\infty \text{ in water}} = \frac{\varphi \text{ of solvent}}{\varphi \text{ of water}}$$

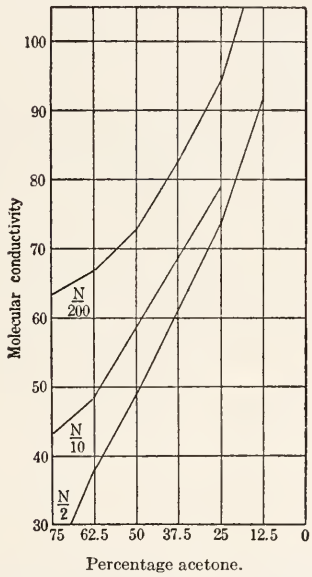


FIG. 50.—Conductivity of rubidium chloride in acetone-water at 25°.

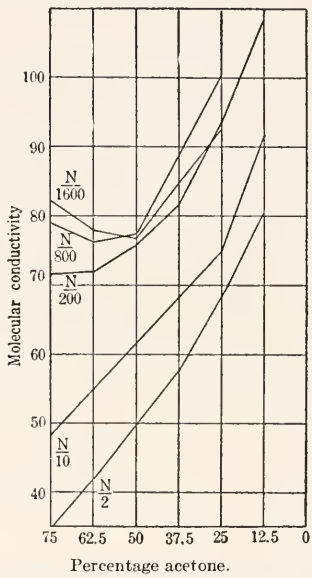


FIG. 51.—Conductivity of rubidium nitrate in acetone-water at 25°.

This would indicate a value of $\mu_\infty = 102$ for rubidium bromide at 25° in "50 per cent" acetone. The molecular conductivity becomes constant at about 80. This indicates either that the equilibrium between ions and molecules becomes constant at $\alpha = 80/102 = 78$ per cent (where α is the percentage dissociation); or that the dissociation is complete at the N/800 dilution, and the molecular conductivity is decreased by a decreasing velocity of the ions. The first alternative seems improbable. The second may seem unlikely in view of the fact that at high concentrations rubidium salts are not appreciably solvated. This, however, is not evidence that there is no solvation at great dilution. And this would seem to be the most probable explanation of the low constant value for μ.

SUMMARY.

The viscosities and conductivities of a number of rubidium salts have been measured in various mixtures of acetone and water.

Rubidium salts increase the viscosity of all mixtures containing a larger percentage of acetone.

The curve representing the fluidities of a solution of any of these salts in the various solvents crosses the curve for the solvents in the neighborhood of the 50 per cent acetone-water mixture.

Negative viscosity coefficients, wherever found, were much smaller than corresponding values in water or glycerol.

The temperature coefficients of fluidity of acetone-water mixtures are very small and decrease with rise in temperature.

The largest temperature coefficients occur in the mixture containing 50 per cent acetone, *i. e.*, the curve representing temperature coefficients passes through a maximum at that point.

Minima in the conductivity curves for rubidium salts correspond to a higher percentage of acetone in the solvent mixtures than do those in the fluidity curves, whereas the two curves are parallel for certain other salts. A possible explanation based on the difference in solubility is offered.

A comparison of the temperature coefficients of conductivity and fluidity shows that these are what is to be expected in the case of a non-solvated salt in a mixture of associated solvents.

A possible indication of solvation of rubidium salts in dilute solutions is pointed out.

CHAPTER VI.

THE CONDUCTIVITY AND VISCOSITY OF CERTAIN RUBIDIUM AND AMMONIUM SALTS IN TERNARY MIXTURES OF GLYCEROL, ACETONE, AND WATER AT 15°, 25°, AND 35°.

By P. B. Davis and W. S. Putnam.

INTRODUCTION.

The fairly extensive investigations of Jones and his collaborators on conductivity and viscosity in the field of mixed solvents, have been brought together and correlated in two elaborate monographs published by the Carnegie Institution of Washington.[1]

By far the greater part of this previous work has been devoted to binary mixtures of the various solvents studied, as well as to the pure solvents themselves. Up to the present, the work has covered very thoroughly the determination of the conductivity and viscosity coefficients of a large number of compounds, both inorganic and organic, in water, and in acetone, glycerol, and the alcohols, as well as in binary mixtures of the latter solvents with one another and with water. Thus far, however, few if any attempts have been made to carry out a systematic study of the behavior of such compounds in ternary mixtures containing the above-named solvents. Such, then, has been the object of the present investigation, which may be taken as the initial step in a series of similar researches.

Before taking up the discussion of this phase of the subject, a short review of the various relations and deductions brought out by previous investigators in the field of mixed solvents, should serve as a fitting introduction to the present work, by calling to mind the various lines of evidence bearing on this subject.

However, since we have been concerned more particularly with glycerol, acetone, and water in this and in previous contributions to the literature on the subject, the review following will be confined to the investigations covering these three important solvents. Moreover, the work in mixed solvents containing the alcohols has recently been carefully reviewed in a previous article.

The first important work in mixed solvents contai ning acetone was that of Jones and Veazey. Prior to their investigations, Bingham and others had made some preliminary determinations of conductivities and fluidities in this solvent along with their work in the alcohols. Thus, Bingham noted the characteristic minima occurring in the conductivity curves for certain salts in acetone-water mixtures, and pointed out that a connection undoubtedly existed between this and a similar phenomenon in the fluidity curves for such mixtures.

[1]Carnegie Inst. Wash. Pubs. Nos. 80 and 180.

Subsequently, McMaster found these minima to be more pronounced at lower temperatures, and corroborated the observations of Bingham regarding the relations between conductivity and fluidity minima in these curves. He also noted and offered a tentative explanation of certain maxima in the curves for acetone-alcohol mixtures.

Although Veazey's work has been fully reviewed in a previous article, it bears directly on the present investigation, since it contains some of the facts earlier established. In addition to confirming the above-mentioned deductions of Bingham, McMaster, and others, Veazey noted and explained the marked increase in viscosity on mixing acetone, as well as the alcohols, with water. This he showed to be due to a mutual diminution in the association of the respective solvents, the resulting mixture having a greater number of ultimate particles and hence a larger viscosity coefficient than either solvent separately. Moreover, Veazey was the first to offer an entirely satisfactory explanation of the phenomenon of negative viscosity noted in certain aqueous solutions by a number of previous investigators, and extended this field to include mixed solvents. His interpretation of this phenomenon is now too well known to require more than the mere statement that it is based on the relations of the molecular volume of the solute to that of the solvent, negative viscosity occurring only when the former is much greater than the latter. This relation is, furthermore, borne out by the position of the cations of the solutes causing negative viscosity at the maxima of the atomic volume curve of Lothar Meyer.

Jones and Schmidt studied glycerol as a solvent, and carried out determinations in both the pure and mixed solvents. They found it well adapted to both conductivity and viscosity work, since, in addition to possessing a high viscosity coefficient, it proved to be a good dissociant, and showed the largest temperature coefficients of conductivity and viscosity of any solvent hitherto employed.

Guy and Jones extended greatly the field opened up by Schmidt, and from a large number of measurements pointed out that molecular conductivities in glycerol are extremely small, but show a regular increase with dilution and rise in temperature. It was also shown that salts having the greatest hydrating power in water possess the largest temperature coefficients of conductivity in glycerol. In mixed solvents Guy and Jones found that conductivities do not follow the law of averages, but are always smaller, and that the ternary electrolytes produce a greater increase in the viscosity of the solvent than the binary electrolytes. Isolated instances of negative viscosity were observed both in glycerol and in certain mixtures of glycerol and water, which led Davis and Jones to make a closer study of this phenomenon.

Davis and Jones, working from the standpoint of negative viscosity, made a careful study of the conduct of rubidium and ammonium salts both in glycerol and in glycerol-water mixtures. They found that

rubidium salts produced a phenomenal lowering of the viscosity of glycerol, while ammonium salts proved to be more closely allied to rubidium than to potassium in their effects on a solvent like glycerol. They also noted minima in certain of the conductivity curves for the more concentrated solutions studied; the conductivity varying directly with the fluidity. In addition to this the percentage increase in fluidity was found to diminish rapidly with rise in temperature and with dilution, and the curves representing fluidity and conductivity in glycerol-water mixtures showed marked similarity. No evidence of positive viscosity of solutions of rubidium salts in glycerol was found, and in the case of mixed solvents only at comparatively high temperatures.

The study of the behavior of rubidium salts in mixed solvents was extended by Davis, Hughes, and Jones to acetone-water mixtures. A marked increase in viscosity was found for all the rubidium salts in the solvents containing the larger percentage of acetone, a phenomenon which this electrolyte had exhibited in none of the solvents previously studied. The curve representing the fluidity of solutions of these salts in the different mixtures was observed to cross that of the solvents in the vicinity of the mixture containing 50 per cent acetone. Negative viscosity coefficients, wherever noted, were much smaller than corresponding values in glycerol-water mixtures. A comparison of the temperature coefficients of fluidity and conductivity showed them to be very similar, and of the order of magnitude to be expected for a non-solvated salt in a mixture of associated solvents. In addition, minima were noted in the conductivity curves for these salts, and were found to correspond to a higher percentage of acetone in the solvent than in the case of similar minima in the fluidity curves.

The important observations on solutions in binary mixtures made by the above-mentioned investigators in this laboratory make it evident that some lines of evidence are desirable, on the behavior of certain salts in ternary mixtures containing the three important solvents discussed, viz, glycerol, acetone, and water. The present investigation, therefore, has been devoted to a study of the behavior of rubidium and ammonium salts which exhibit negative viscosity to a high degree in many pure solvents and their binary mixtures, in a new series of solvents which contain varying proportions of glycerol, acetone, and water.

EXPERIMENTAL.

APPARATUS.

Thermostats.—As in previous years, it has been our constant aim to bring to as near perfection as possible this fundamental part of the apparatus. With this in view, a new type of thermostat (fig. 52 A) has been devised suitable both for conductivity and viscosity determinations, or for reaction velocity work; and three such baths have been recently installed and put into full working order (Plate I). These thermostats are of about 60 liters capacity and are substantially con-

structed of copper. Gas is employed as a means of maintaining the desired temperature, the heat being applied to a heavy iron pipe (fig. 52 A-H) outside the circumference of the bath, and through this pipe water is kept circulating by the propellers. Thus only a small portion of the water in the thermostat comes into immediate contact with the heated surface, being subsequently mixed with the main body of water, thereby securing much more even distribution of heat.

The improved type of mercury regulator described by Davis and Hughes was used to operate the relays (fig. 52 C) controlling the gas-supply to the micro-burners of the thermostats. A new type of toluene regulator suitable for a wide range of temperature has been constructed (fig. 52 B). With the above improved apparatus, temperature regulation to within 0.01° was easily maintained over any length of time throughout the work, and with a reasonable amount of attention regulation to 0.005° was attained. (See fig. 52 for details of the system.)

The hot-air engines formerly used as a source of power for the stirrers have been discarded in favor of the electric motor, which gives greater freedom from vibrations and permits the maintainence of constant temperature in the baths both day and night. Both belt and friction drive were used to transmit power from motor to stirrers, a 1-12 horse-power direct-current motor serving to operate all five thermostats.

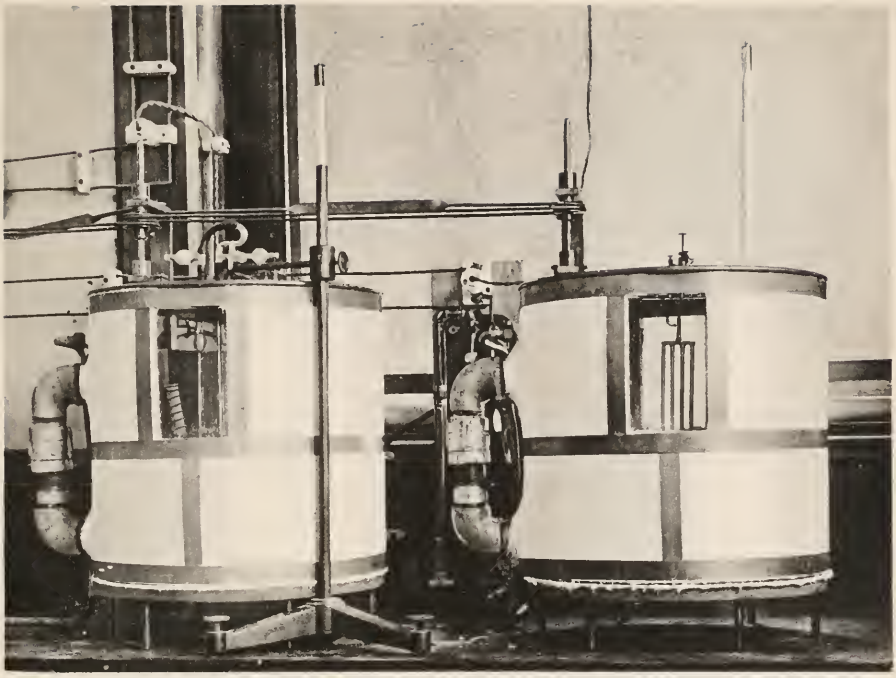
Conductivity Apparatus.—The conductivity apparatus used in this investigation was identical with that employed for our recent work in acetone-water mixtures; the methods of obtaining duplicate readings, system of wiring, and similar details remaining exactly the same as in the earlier work. The conductivity cells also were of the type now generally employed here for such work, and have been fully described elsewhere. All the instruments used were carefully calibrated at regular intervals or compared with standards.

Viscosity Apparatus.—The usual type of viscosity apparatus as developed and improved here was used throughout this work. Special care was exercised both in calibrating all the instruments and in guarding against external jars and vibrations.

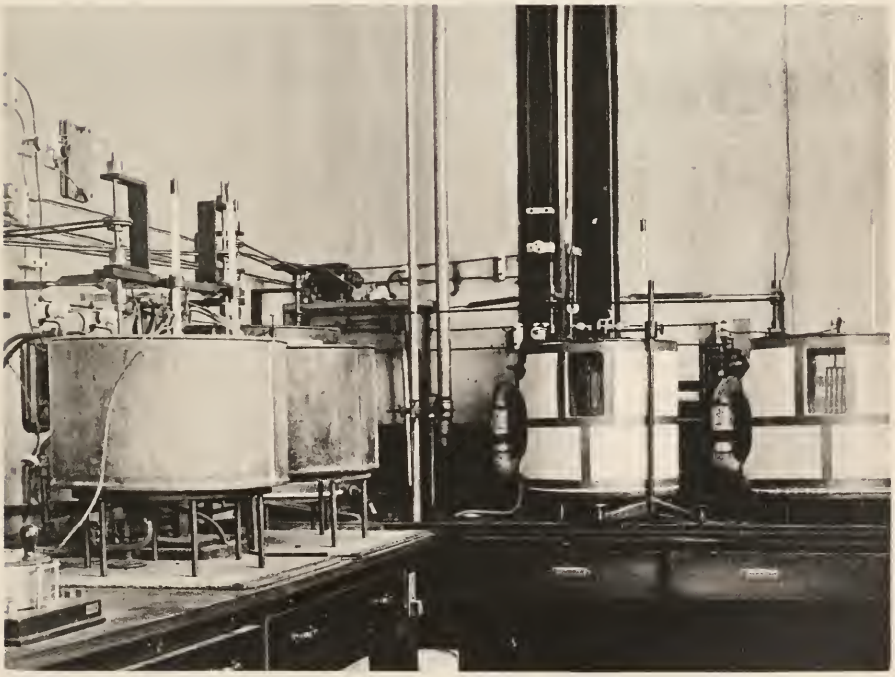
Volumetric Apparatus.—All flasks were carefully calibrated by repeated weighings to hold aliquot parts of the true liter at 20°; and solvents and solutions were brought to within 0.1° of this temperature before being diluted to the calibration mark. All pipettes used in making up the solvents were standardized to drain a definite amount of each component at 20°, the mean of a number of weighings being taken as the drainage capacity of the respective instruments.

SOLVENTS.

The glycerol used in these ternary mixtures was Kahlbaum's 1.26, with a mean specific gravity of 1.257 at 25° and a specific conductivity of 0.6×10^{-7} at the same temperature.



Enlarged View of New Form of Thermostat. For diagram and detailed description see Fig. 52.



General View of Constant Temperature Apparatus for Viscosity and Conductivity Investigations showing arrangement, methods of stirring, heating, regulating, etc.

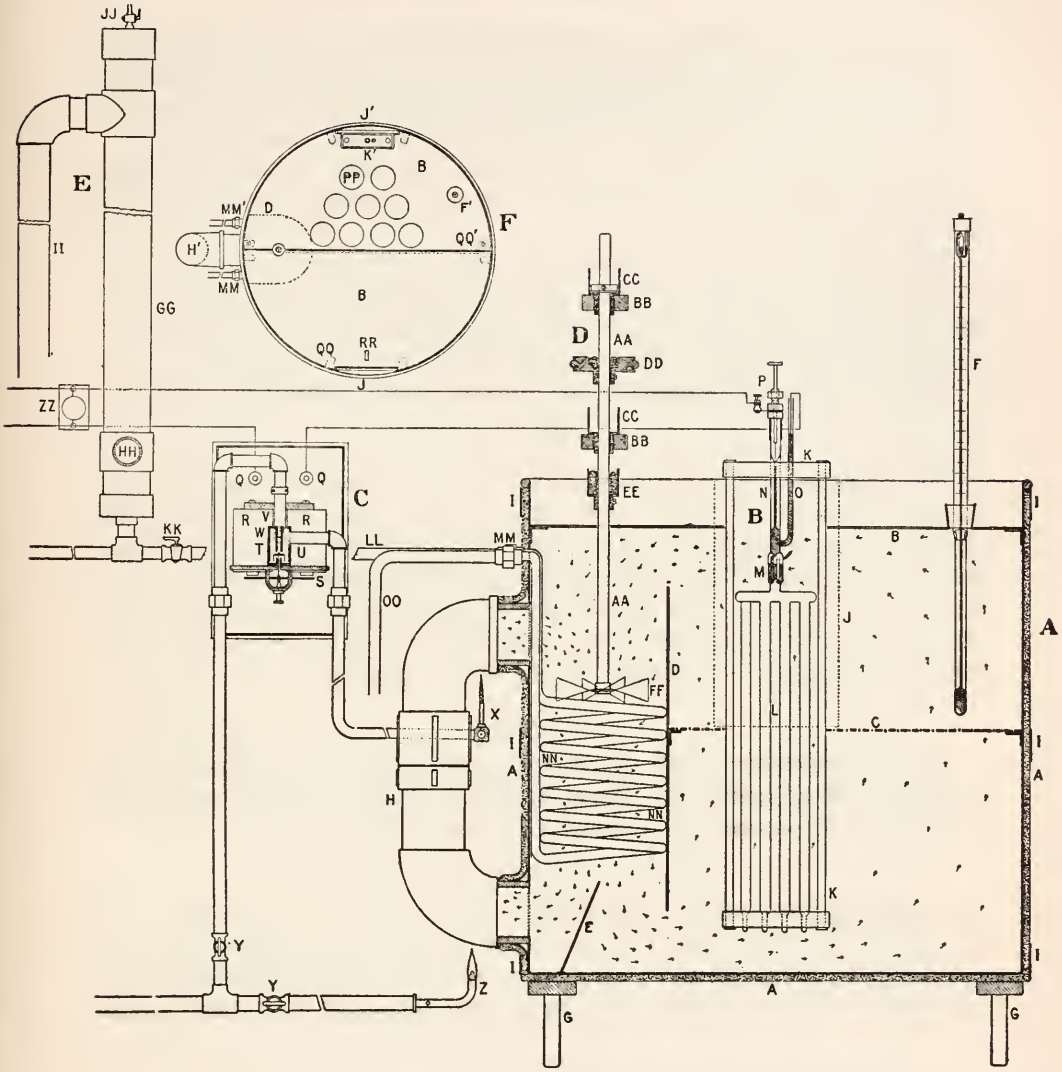


FIG. 52.—Constant Temperature Apparatus for Conductivity and Viscosity Investigations.

A. Sixty-liter bath of 20-oz. copper: (A) Asbestos insulation; (B) sheet-brass cover; (C) woven-wire grid; (D) semicircular diaphragm; (E) deflector to divert part of the water into heater pipes; (F) thermometer; (G) tripod; (H) galvanized-iron heater pipes attached with $1\frac{1}{2}$-inch brass nipples; (I) brass bands supporting insulation; (J) outline of windows.

B. Thermostat: (K) Holder; (L) toluol reservoir tubes with $\frac{1}{4}$ mm. walls; (M) expansion chamber partially filled with mercury; (N) 1.5 mm. capillary; (O) side arm with sealed-in platinum contact; (P) platinum tipped contact needle.

C. Gas-flow regulator (based on "steel block" devised by E. E. Reid, Amer. Chem. Journ., 1909, **41**, 151): (Q) Binding posts to coils; (R) magnet coils; (S) armature; (T) steel valve chamber; (U) plunger with rubber washer and mercury seal working against end of gas-supply pipe (V) and wired to armature (S); (W) needle valve to regulate size of pilot flame; (X) micro-burner with needle valve; (Y) gas-cocks to relay and rough heater (Z); (ZZ) high-voltage lamp spanning spark-gap of thermostat.

D. Stirring mechanism: (AA) Shaft; (BB) ⊏-shaped bracket; (CC) oil cups and bearings; (DD) pulley with oil trap filled with waste; (EE) oil trap; (FF) six-bladed propeller.

E. Cooling system: (GG) Standpipe; (HH) supply; (II) overflow; (JJ) petcock in cap; (KK) regulating valve to coils; (LL) inlet pipe to coils; (MM) interchangeable unions (here ice or hot water coils may be inserted for very low or high temperatures); (NN) cooling coils; (OO) waste pipe.

F. Diagram of top (smaller scale): (B), (D), (F), (H), (J), and (K) the same as in A; (MM) same as in E; (PP) apertures in cover for conductivity cells; (QQ) lugs supporting cover; (RR) handle to removable section of cover.

The acetone was dried over calcium chloride for at least a week before using and was then redistilled several times immediately before making up the mixed solvents. It had a mean specific gravity of 0.787 at 25°, and a specific conductivity of about 4×10^{-7} at that temperature.

The conductivity water was obtained by the method of Jones, McKay, and Schmidt, and had a mean specific conductivity of 1.5×10^{-6} at 25°.

The mixed solvents were prepared by mixing one or two parts of each of the above components with varying proportions of the other two. Seven such combinations proved to be possible, and were prepared for solvents in one-liter quantities immediately before using.

The specific data relating to each solvent are to be found in table 33.

SALTS.

The rubidium and ammonium salts were all carefully recrystallized from conductivity water, precipitated and washed with absolute alcohol, then dried first in the steam oven, and finally pulverized and heated in an air-bath at the most favorable temperature for the salt in question. By this procedure, products of an exceptional purity were obtained, and even in the case of ammonium iodide the concentrated solutions became only slightly tinted after standing.

SOLUTIONS.

All solutions were made up as described by Davis and Hughes; the concentrated solutions by direct weighing, the others by successive dilutions. All operations were carried out at 20°.

PROCEDURE.

Measurements both of conductivity and viscosity were made at 15°, 25°, and 35°. The data were calculated in the usual way, tables of constants and the use of a calculating machine greatly facilitating the operation. The viscosity coefficients were obtained from the formula

$$\frac{\eta}{\eta_0} = \frac{st}{s_0 t_0}$$

where η_0, s_0, and t_0 are the viscosity, density, and time of flow of pure water, and η, s, and t the corresponding values for the liquid in question in any given viscosimeter.

Fluidity, represented by ϕ, is equal to $\frac{1}{\eta}$. The temperature coefficients in conductivity units represent the actual increase in molecular conductivity per degree rise in temperature.

Per cent temperature coefficients, both of conductivity and fluidity, were calculated from the formula:

$$\text{Temp. coeff. of } (\mu \text{ or } \phi) = \frac{1}{(\mu \text{ or } \phi)_{t_1}} \cdot \frac{(\mu \text{ or } \phi)\, t_2 - (\mu \text{ or } \phi)\, t_1}{t_2 - t_1}$$

VISCOSITY DATA.

TABLE 33.—*Density, specific conductivity, viscosity and fluidity of ternary mixtures of glycerol, acetone, and water* (G, A, W).

Mixtures of			15°				25°				35°			
G	A	W	d	μ	η	ϕ	d	μ	η	ϕ	d	μ	η	ϕ
1	2	2	1.0063	0.00343	0.03539	28.26	0.9984	0.00468	0.02530	39.53	0.9902	0.00613	0.01888	52.87
1	2	1	1.0064	.00215	.03842	26.03	0.9959	.00294	.02738	36.52	0.9874	.00390	.02035	49.14
1	1	2	1.0443	.00368	.04107	23.83	1.0377	.00508	.02951	33.89	1.0308	.00676	.02174	46.00
1	1	1	1.0515	.00237	.06379	15.68	1.0439	.00332	.04349	23.00	1.0354	.00453	.04116	32.09
2	1	2	1.0905	.00233	.08090	12.36	1.0839	.00333	.05414	18.47	1.0768	.00458	.03826	26.14
2	2	1	1.0534	.00139	.08901	11.24	1.0453	.00202	.05954	16.80	1.0363	.00283	.05954	23.94
2	1	1	1.1072	.00132	.15296	6.54	1.0998	.00202	.09706	10.31	1.0923	.00293	.06474	15.45

TABLE 34.—*Viscosity and fluidity of salts in the 1–2–2 solvent (glycerol 1, acetone 2, water 2), at 15°, 25°, 35°.*

Mol. conc.	Viscosities.			Fluidities.			Temp. coeff.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
RUBIDIUM BROMIDE IN THE 1–2–2 SOLVENT.								
0.50	0.03571	0.02603	0.01950	28.00	38.42	51.28	0.0335	0.0371
.25	.03608	.02555	.01959	27.72	39.14	51.05	.0412	.0304
.10	.03506	.02529	.01887	28.52	39.54	52.99	.0386	.0340
Solv.	.03539	.02530	.01888	28.26	39.53	52.87	.0399	.0337
RUBIDIUM IODIDE IN THE 1–2–2 SOLVENT.								
0.50	0.03477	0.02532	0.01921	28.76	39.49	52.06	0.0373	0.0318
.25	.03471	.02494	.01850	28.81	40.10	54.05	.0390	.0348
.10	.03551	.02550	.01888	28.16	39.22	52.97	.0392	.0350
Solv.	.03539	.02530	.01888	28.26	39.53	52.87	.0399	.0337
AMMONIUM IODIDE IN THE 1–2–2 SOLVENT.								
0.50	0.03486	0.02552	0.01954	28.69	39.19	51.98	0.0366	0.0326
.25	.03483	.02503	.01860	28.71	39.95	53.74	.0389	.0345
.10	.03540	.02548	.01913	28.25	39.25	52.27	.0389	.0331
Solv.	.03539	.02530	.01888	28.26	39.53	52.87	.0399	.0337

TABLE 35.—*Viscosity and fluidity of salts in the 1–2–1 solvent (glycerol 1, acetone 2, water 1), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 1–2–1 SOLVENT.

Mol. conc.	Viscosities.			Fluidities.			Temp. coeff.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
0.50	0.04089	0.02950	0.02228	24.45	33.90	44.88	0.0387	0.0324
.25	.04004	.02895	.02180	24.98	34.54	45.87	.0383	.0325
.10	.03950	.02837	.02134	25.32	35.25	46.86	.0392	.0329
Solv.	.03842	.02738	.02035	26.03	36.52	49.14	.0403	.0345
RUBIDIUM IODIDE IN THE 1–2–1 SOLVENT.								
0.50	0.03998	0.02878	0.02163	25.01	34.74	46.23	0.0389	0.0331
.25	.03960	.02873	.02162	25.25	34.81	46.25	.0377	.0300
.10	.03930	.02819	.02127	25.45	35.47	47.01	.0394	.0328
Solv.	.03842	.02738	.02035	26.03	36.52	49.14	.0403	.0345
AMMONIUM BROMIDE IN THE 1–2–1 SOLVENT.								
0.50	0.04090	0.02941	0.02214	24.45	34.00	45.17	0.0391	0.0328
.25	.04064	.02917	.02196	24.61	34.28	45.54	.0394	.0328
.10	.03830	.02843	.02132	26.11	35.17	46.90	.0347	.0333
Solv.	.03842	.02738	.02035	26.03	36.52	49.14	.0403	.0345
AMMONIUM IODIDE IN THE 1–2–1 SOLVENT.								
0.50	0.04032	0.02880	0.02166	24.80	34.72	46.17	0.0400	0.0330
.25	.03976	.02864	.02154	25.15	34.92	46.43	.0388	.0330
.10	.03928	.02818	.02112	25.46	35.49	47.35	.0394	.0334
Solv.	.03842	.02738	.02035	26.03	36.52	49.14	.0403	.0345

TABLE 36.—*Viscosity and fluidity of salts in the 1–1–2 solvent (glycerol 1, acetone 1, water 2), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 1–1–2 SOLVENT.

Mol. conc.	Viscosities.			Fluidities.			Temp. coeff.	
	η 15°	η 25°	η 35°	δ 15°	δ 25°	δ 35°	15 to 25°	25 to 35°
0.50	0.04041	0.02857	0.02122	24.75	35.00	47.13	0.0414	0.0346
.25	.04131	.02926	.02175	24.21	34.18	45.98	.0412	.0345
.10	.04162	.02940	.02170	24.08	34.01	46.08	.0412	.0354
Solv.	.04107	.02951	.02174	23.83	33.89	46.00	.0423	.0358
RUBIDIUM IODIDE IN THE 1–1–2 SOLVENT.								
0.50	0.03923	0.02781	0.02062	25.49	35.96	48.50	0.0416	0.0349
.25	.04068	.02894	.02152	24.58	34.55	46.47	.0406	.0345
.10	.04140	.02905	.02166	24.15	34.42	46.17	.0425	.0340
Solv.	.04107	.02951	.02174	23.83	33.89	46.00	.0423	.0358
AMMONIUM IODIDE IN THE 1–1–2 SOLVENT.								
0.50	0.03926	0.02792	0.02060	25.47	35.82	48.54	0.0406	0.0355
.25	.04075	.02885	.02149	24.44	34.66	46.53	.0418	.0342
.10	.04148	.02915	.02153	24.11	34.31	46.23	.0423	.0348
Solv.	.04107	.02951	.02174	23.83	33.89	46.00	.0423	.0358
AMMONIUM BROMIDE IN THE 1–1–2 SOLVENT.								
0.50	0.04050	0.02881	0.02126	24.69	34.71	47.04	0.0406	0.0355
.25	.04130	.02933	.02173	24.21	34.09	46.02	.0408	.0350
.10	.04170	.02933	.02176	23.98	34.09	45.96	.0422	.0348
Solv.	.04107	.02951	.02174	23.83	33.89	46.00	.0423	.0358

TABLE 37.—*Viscosity and fluidity of salts in the 1–1–1 solvent (glycerol 1, acetone 1, water 1), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 1–1–1 SOLVENT.

Mol. conc.	Viscosities.			Fluidities.			Temp. coeff.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
0.50	0.06371	0.04404	0.03196	15.70	22.71	31.29	0.0447	0.0378
.25	.06358	.04380	.03158	15.73	22.83	31.67	.0452	.0387
.10	.06335	.04309	.03084	15.79	23.21	32.43	.0470	.0397
Solv.	.06379	.04349	.03116	15.68	23.00	32.09	.0467	.0395
RUBIDIUM IODIDE IN THE 1–1–1 SOLVENT.								
0.50	0.06239	0.04402	0.03209	16.03	22.72	31.16	0.0417	0.0372
.25	.06234	.04307	.03085	16.04	23.22	32.42	.0447	.0396
.10	.06282	.04340	.03128	15.92	23.04	31.97	.0447	.0387
Solv.	.06379	.04349	.03116	15.68	23.00	32.09	.0467	.0395
AMMONIUM BROMIDE IN THE 1–1–1 SOLVENT.								
0.50	0.06353	0.04397	0.03190	15.74	22.74	31.35	0.0445	0.0378
.25	.06338	.04358	.03143	15.78	22.05	31.82	.0454	.0385
.10	.06317	.04304	.03088	15.83	23.23	32.38	.0468	.0394
Solv.	.06379	.04349	.03116	15.68	23.00	32.09	.0467	.0395
AMMONIUM IODIDE IN THE 1–1–1 SOLVENT.								
0.50	0.06119	0.04247	0.03054	16.34	23.55	32.74	0.0435	0.0391
.25	.06288	.04333	.03137	15.90	23.08	31.88	.0451	.0381
.10	.06338	.04449	.03153	15.78	22.48	31.72	.0425	.0411
Solv.	.06379	.04349	.03116	15.68	23.00	32.09	.0467	.0395

TABLE 38.—*Viscosity and fluidity of salts in the 2–1–2 solvent (glycerol 2, acetone 1, water 2), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 2–1–2 SOLVENT.

Mol. conc.	Viscosities.			Fluidities.			Temp. coeff.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
0.50	0.07739	0.05334	0.03804	12.92	18.75	26.29	0.0450	0.0402
.25	.08014	.05355	.03782	12.48	18.67	26.44	.0497	.0416
.10	.08107	.05432	.03829	12.34	18.42	26.12	.0493	.0418
Solv.	.08090	.05414	.03826	12.36	18.47	26.14	.0494	.0415
RUBIDIUM IODIDE IN THE 2–1–2 SOLVENT.								
0.50	0.07575	0.05165	0.03693	13.20	19.36	27.08	0.0467	0.0398
.25	.07730	.05218	.03654	12.94	19.16	27.37	.0482	.0427
.10	.07967	.05370	.03782	12.55	18.62	26.44	.0484	.0419
Solv.	.08090	.05414	.03826	12.36	18.47	26.14	.0494	.0415
AMMONIUM BROMIDE IN THE 2–1–2 SOLVENT.								
0.50	0.07739	0.05202	0.03702	12.92	19.22	27.01	0.0488	0.0405
.25	.07934	.05366	.03821	12.60	18.64	26.17	.0479	.0404
.10	.08054	.05320	.03763	12.42	18.80	26.57	.0514	.0418
Solv.	.08090	.05414	.03826	12.36	18.47	26.14	.0494	.0415
AMMONIUM IODIDE IN THE 2–1–2 SOLVENT.								
0.50	0.07545	0.05175	0.03683	13.25	19.32	27.15	0.0458	0.0405
.25	.07729	.05206	.03660	12.94	19.21	27.32	.0484	.0423
.10	.07854	.05417	.03855	12.73	18.46	25.94	.0450	.0405
Solv.	.08090	.05414	.03826	12.36	18.47	26.14	.0494	.0415

TABLE 39.—*Viscosity and fluidity of salts in the 2–2–1 solvent (glycerol 2, acetone 2, water 1), at 15°, 25°, 35°.*

AMMONIUM BROMIDE IN THE 2–2–1 SOLVENT.

Mol. conc.	Viscosities.			Fluidities.			Temp. coeff.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
0.50	Gave a non-homogeneous solution. Acetone salted out.						.....	.....
.25	0.08989	0.06071	0.04359	11.12	16.47	22.94	0.0481	0.0392
.10	.08938	.05906	.04178	11.19	16.94	23.83	.0514	.0407
Solv.	.08901	.05954	.04177	11.24	16.80	23.94	.0495	.0426
AMMONIUM IODIDE IN THE 2–2–1 SOLVENT.								
0.50	0.08985	0.06493	0.04867	11.13	15.40	20.55	0.0384	0.0336
.25	.08939	.06282	.04437	11.19	15.92	22.54	.0423	.0416
.10	.08915	.06290	.04371	11.22	15.90	22.88	.0418	.0502
Solv.	.08901	.05954	.04177	11.24	16.80	23.94	.0495	.0426

TABLE 40.—*Viscosity and fluidity of salts in the 2–1–1 solvent (glycerol 2, acetone 1, water 1), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 2–1–1 SOLVENT.

Mol. conc.	Viscosities.			Fluidities.			Temp. coeff.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
0.50	0.15066	0.09583	0.06512	6.64	10.44	15.36	0.0572	0.0491
.25	.15388	.09781	.06633	6.50	10.22	15.08	.0573	.0475
.10	.15462	.09812	.06623	6.47	10.19	15.10	.0576	.0481
Solv.	.15296	.09706	.06474	6.54	10.31	15.45	.0576	.0499
RUBIDIUM IODIDE IN THE 2–1–1 SOLVENT.								
0.50	0.14625	0.09322	0.06316	6.84	10.73	15.83	0.0569	0.0476
.25	.15194	.09682	.06557	6.68	10.33	15.25	.0546	.0476
.10	.15408	.09779	.06589	6.49	10.23	15.18	.0576	.0482
Solv.	.15296	.09706	.06474	6.54	10.31	15.45	.0576	.0499
AMMONIUM BROMIDE IN THE 2–1–1 SOLVENT.								
0.50	0.15177	0.09650	0.06575	6.63	10.36	15.21	0.0562	0.0468
.25	.15417	.09816	.06652	6.49	10.19	15.03	.0571	.0476
.10	.15550	.09814	.06624	6.45	10.19	15.10	.0579	.0482
Solv.	.15296	.09706	.06474	6.54	10.31	15.45	.0576	.0499
AMMONIUM IODIDE IN THE 2–1–1 SOLVENT.								
0.50	0.14709	0.09366	0.06352	6.80	10.68	15.74	0.0570	0.0475
.25	.15211	.09703	.06559	6.57	10.31	15.25	.0568	.0479
.10	.15410	.09757	.06588	6.49	10.25	15.08	.0579	.0471
Solv.	.15296	.09706	.06474	6.54	10.31	15.45	.0576	.0499

CONDUCTIVITY DATA.

TABLE 41.—*Molecular conductivities and temperature coefficients of salts in the 1–2–2 solvent (glycerol 1, acetone 2, water 2), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 1–2–2 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Cond. units.	
	μ_v 15°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	23.50	30.93	39.20	0.0316	0.0267	0.743	0.827
4	23.14	29.33	35.92	.0267	.0225	.619	.659
10	25.87	32.06	39.39	.0239	.0242	.619	.659
50	29.10	37.09	47.57	.0275	.0283	.799	1.048
200	30.60	39.84	50.55	.0302	.0269	.924	1.071
RUBIDIUM IODIDE IN THE 1–2–2 SOLVENT.							
2	25.90	33.99	42.76	0.0312	0.0258	0.809	0.877
4	25.74	33.58	43.85	.0305	.0306	.784	1.027
10	27.03	36.75	.....	.0360	.....	.972	.....
50	30.08	40.08	51.10	.0332	.0275	1.000	1.102
200	30.61	41.00	52.49	.0339	.0280	1.039	1.149
AMMONIUM IODIDE IN THE 1–2–2 SOLVENT.							
2	25.81	33.87	42.86	0.0312	0.0265	0.806	0.899
4	26.60	34.99	44.44	.0315	.0270	.839	.945
10	28.72	38.00	48.70	.0323	.0282	.928	1.070
50	29.94	39.78	50.73	.0329	.0275	.984	1.095
200	31.14	41.69	53.60	.0339	.0286	1 055	1.101

TABLE 42.—*Molecular conductivities and temperature coefficients of salts in the 1–2–1 solvent (glycerol 1, acetone 2, water 1), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 1–2–1 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Cond. units.	
	μ_v 15°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	14.78	19.35	24.49	0.0309	0.0266	0.457	0.514
4	15.82	20.74	26.45	.0311	.0275	.492	.571
10	17.24	22.69	29.12	.0316	.0288	.545	.643
50	19.10	25.50	32.87	.0335	.0289	.640	.737
RUBIDIUM IODIDE IN THE 1–2–1 SOLVENT.							
2	18.33	23.81	30.24	0.0299	0.0270	0.548	0.643
4	19.00	24.68	31.41	.0299	.0273	.568	.673
10	20.00	26.22	33.74	.0311	.0287	.622	.752
50	21.40	29.25	36.51	.0322	.0291	.688	.823
200	22.56	29.85	38.69	.0323	.0296	.729	.884
800	24.23	32.80	42.00	.0354	.0280	.857	.920
AMMONIUM BROMIDE IN THE 1–2–1 SOLVENT.							
2	15.94	19.72	24.94	0.0311	0.0265	0.468	0.522
4	15.41	20.45	26.24	.0327	.0283	.504	.579
10	17.34	22.81	29.23	.0315	.0282	.547	.642
50	19.28	25.82	33.22	.0339	.0287	.654	.740
AMMONIUM IODIDE IN THE 1–2–1 SOLVENT.							
2	18.23	23.66	30.28	0.0298	0.0283	0.543	0.662
4	18.80	24.67	31.26	.0312	.0267	.587	.659
10	19.88	26.36	33.54	.0326	.0272	.648	.718

TABLE 43.—*Molecular conductivities and temperature coefficients of salts in the 1–1–2 solvent (glycerol 1, acetone 1, water 2), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 1–1–2 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Cond. units.	
	μ_v 15°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	26.35	34.62	44.31	0.0314	0.0280	0.827	0.969
4	25.59	33.45	41.99	.0307	.0255	.786	.845
10	28.02	37.23	48.03	.0329	.0290	.921	1.080
50	28.75	39.86	51.71	.0386	.0297	1.111	1.185
RUBIDIUM IODIDE IN THE 1–1–2 SOLVENT.							
2	27.42	35.96	45.94	0.0311	0.0278	0.854	0.998
4	26.80	35.39	45.36	.0320	.0282	.859	.997
10	28.17	37.52	48.67	.0332	.0297	.935	1.115
50	29.17	38.98	51.16	.0336	.0312	.981	1.218
800	32.40	43.92	57.46	.0356	.0308	1.152	1.354
AMMONIUM BROMIDE IN THE 1–1–2 SOLVENT.							
2	26.57	35.19	44.71	0.0324	0.0263	0.862	0.952
4	25.98	34.29	43.03	.0320	.0255	.831	.874
10	27.85	37.20	47.92	.0336	.0288	.935	1.072
50	29.40	39.48	51.17	.0343	.0296	1.008	1.169
800	31.99	43.36	55.44	.0349	.0279	1.117	1.208
AMMONIUM IODIDE IN THE 1–1–2 SOLVENT.							
2	27.54	35.86	46.36	0.0302	0.0293	0.832	1.050
4	26.40	35.22	45.21	.0334	.0284	.882	.999
10	27.93	37.62	48.68	.0347	.0294	.969	1.106
50	28.88	38.97	50.67	.0347	.0300	1.001	1.170
200	30.82	41.47	54.02	.0346	.0303	1.065	1.255
800	31.86	43.01	56.34	.0350	.0310	1.115	1.333

TABLE 44.—*Molecular conductivities and temperature coefficients of salts in the 1–1–1 solvent (glycerol 1, acetone 1, water 1), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 1–1–1 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Cond. units.	
	μ_v 15°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	15.22	20.56	26.80	0.0351	0.0304	0 534	0.624
4	15.68	21.20	28.02	.0352	.0322	552	.682
10	16.51	22.53	29.71	.0365	.0319	602	.718
50	17.67	24.41	32.33	.0381	.0325	674	.794
200	18.19	25.30	33.43	.0391	.0321	11	.813
RUBIDIUM IODIDE IN THE 1–1–1 SOLVENT.							
2	16.07	21.95	28.81	0.0366	0.0313	0.588	0.686
4	16.67	22.93	29.98	.0375	.0307	.626	.705
10	17.65	24.24	31.90	.0316	.0316	.659	.766
50	.....	.....	.....	.....	.....	.....	.....
200	19.23	26.73	34.09	.0389	.0275	.750	.736

TABLE 44.—*Molecular conductivities and temperature coefficients of salts in the 1–1–1 solvent (glycerol 1, acetone 1, water 1), at 15°, 25°, 35°.*—Continued.

AMMONIUM BROMIDE IN THE 1–1–1 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Cond. units.	
	μ_v 16°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	15.21	20.57	27.11	0.0352	0.0418	0.536	0.654
4	15.71	21.41	28.45	.0363	.0329	.570	.704
10	16.56	22.58	30.03	.0363	.0326	.602	.745
50	17.84	24.59	32.88	.0378	.0337	.675	.829
200	18.50	25.52	34.13	.0379	.0338	.702	.863
AMMONIUM IODIDE IN THE 1–1–1 SOLVENT.							
2	15.57	20.51	25.87	0.0317	0.0261	0.494	0.536
4	16.86	23.04	30.35	.0366	.0317	.618	.731
10	17.43	23.68	31.84	.0359	.0345	.625	.816
50	17.87	24.38	33.20	.0364	.0362	.651	.882
200	18.72	26.05	34.67	.0392	.0331	.733	.862

TABLE 45.—*Molecular conductivities and temperature coefficients of salts in the 2–1–2 solvent (glycerol 2, acetone 1, water 2), at 15°, 25°, 35°.*

RUBIDIUM BROMIDE IN THE 2–1–2 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cnet.		Cond. units.	
	μ_v 15°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to .5°	25 to 35°
2	15.04	20.75	27.45	0.0380	0.0323	0.571	0.670
4	15.55	21.59	28.66	.0388	.0327	.604	.707
10	16.66	22.99	30.30	.0380	.0318	.633	.731
50	17.54	24.58	32.92	.0401	.0339	.704	.834
200	18.15	25.54	34.47	.0407	.0350	.739	.893
RUBIDIUM IODIDE IN THE 2–1–2 SOLVENT.							
2	15.32	21.29	28.25	0.0390	0.0328	0.597	0.699
4	15.57	21.78	29.02	.0399	.0332	.621	.724
10	16.42	22.98	30.58	.0399	.0331	.656	.760
50	17.07	24.06	32.38	.0409	.0346	.699	.832
200	17.12	24.24	32.66	.0416	.0347	.712	.842
AMMONIUM BROMIDE IN THE 2–1–2 SOLVENT.							
2	15.55	21.59	28.55	0.0388	0.0322	0.604	0.696
4	15.60	21.52	28.86	.0379	.0341	.592	.734
10	16.16	22.52	30.13	.0394	.0338	.636	.761
50	16.92	23.78	32.08	.0406	.0349	.686	.830
200	17.59	24.73	33.25	.0406	.0345	.714	.852
AMMONIUM IODIDE IN THE 2–1–2 SOLVENT.							
2	15.58	21.71	28.79	0.0393	0.0326	0.613	0.708
4	15.80	22.05	29.39	.0396	.0333	.625	.734
10	16.48	22.61	30.13	.0372	.0333	.613	.752
50	17.11	24.46	32.88	.0430	.0344	.735	.842
200	17.34	24.57	33.16	.0417	.0350	.723	.859

TABLE 46.—*Molecular conductivities and temperature coefficients of salts in the 2–2–1 solvent (glycerol 2, acetone 2, water 1), at 15°, 25°, 35°.*

AMMONIUM BROMIDE IN THE 2–2–1 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Cond. units.	
	μ_v 15°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	Gave a non-homogeneous solution. Acetone salted out.						
4	9.09	12.44	16.85	0.0369	0.0355	0.335	0.441
10	9.81	13.71	18.42	.0399	.0344	.391	.471
50	10.62	14.99	20.43	.0411	.0363	.437	.544
200	11.21	15.93	21.77	.0421	.0367	.472	.584
AMMONIUM IODIDE IN THE 2–2–1 SOLVENT.							
2	9.87	13.23	16.95	0.0340	0.0281	0.336	0.372
4	10.63	14.75	19.68	.0388	.0334	.412	.493
10	11.40	15.80	21.11	.0386	.0336	.440	.531
50	12.18	16.97	23.12	.0393	.0362	.479	.615
200	12.40	17.50	23.69	.0411	.0354	.510	.619

TABLE 47.—*Molecular conductivities and temperature coefficients of salts in the 2-1-1 solvent (glycerol 2, acetone 1, water 1), at 15°, 25°, 35°.*

AMMONIUM BROMIDE IN THE 2–1–1 SOLVENT.

V	Molecular conductivities.			Temperature coefficients.			
				Per cent.		Cond. units.	
	μ_v 15°	μ_v 25°	μ_v 35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	7.91	11.20	15.82	0.0416	0.0413	0.329	0.462
4	7.83	11.25	15.61	.0437	.0388	.342	.436
10	8.23	12.06	16.88	.0465	.0400	.383	.482
50	8.56	12.67	17.80	.0480	.0405	.411	.513
800	9.19	13.55	19.34	.0474	.0427	.436	.579
AMMONIUM IODIDE IN THE 2–1–1 SOLVENT.							
2	8.08	11.79	16.46	0.0459	0.0396	0.371	0.467
4	8.16	11.97	16.77	.0467	.0401	.381	.480
10	8.38	12.29	17.31	.0467	.0408	.391	.502
50	8.87	13.10	18.55	.0477	.0416	.423	.545
800	8.69	12.84	18.36	.0478	.0430	.415	.552
RUBIDIUM BROMIDE IN THE 2–1–1 SOLVENT.							
2	7.62	11.19	15.53	0.0469	0.0388	0.357	0.434
4	7.68	11.19	15.57	.0453	.0395	.348	.441
10	8.10	11.93	16.74	.0473	.0403	.383	.481
50	8.50	12.55	17.72	.0476	.0412	.405	.517
800	.....	12.62	17.83	.....	.0413	.....	.521
RUBIDIUM IODIDE IN THE 2–1–1 SOLVENT.							
2	7.92	11.31	16.18	0.0420	0.0433	0.333	0.487
4	8.02	11.79	16.52	.0470	.0401	.377	.473
10	8.26	12.16	17.10	.0472	.0406	.390	.494
50	8.53	12.67	17.93	.0485	.0415	.414	.526
800	9.26	13.99	20.01	.0511	.0430	.473	.602

DISCUSSION OF RESULTS.

As in our preceding work with rubidium and ammonium salts in glycerol and acetone and their binary mixtures with water, parallel investigations in viscosity and conductivity have been carried out.

We have obtained measurements with both concentrated and moderately dilute solutions over a wide range of ternary mixtures of the three solvents employed. Although glycerol and acetone of themselves are immiscible, the addition of about 20 per cent water gives a perfectly homogeneous liquid which corresponds to our 2–2–1 solvent. However, it should be noted that in this solvent which contains the lowest percentage of water in the series, it was impossible to obtain concentrated solutions of the ammonium salts while the rubidium salts failed to go into solution at concentrations above 1/200 N., since the acetone immediately separated out giving a non-homogeneous solution.

As previously noted, table 33 shows the specific data relating to the various mixtures, viz, the density, specific conductivity, viscosity, and fluidity at all three temperatures studied. Reference to it will show that, *e. g.*, at 25°, the standard comparison temperature, the solvents possess densities ranging from 0.9984 for the 1–2–2 mixture to 1.0998 for the 2–1–1, while the viscosities for the same solvents vary between 0.02530 and 0.09706. Thus, the viscosities for the two extremes in the series lie between those of 25 and 50 per cent glycerol and water (0.02017 − 0.06021) for the former and between the 75 and 50 per cent (0.0135 − 0.06021) for the latter extreme. The values, however, lie in both cases nearest the least viscous glycerol mixture.

The specific conductivity of the 1–1–1 solvent is about 3,000 times that calculated by averaging the specific conductivities of each of the constituents. Jones and Davis[1] have noted that in mixtures of glycerol and water containing 50 and 25 per cent glycerol, the specific conductivity was higher than for pure water. Their explanation is that the $\overline{OH}$ ion is split off; *i. e.*, the glycerol is dissociated by the action of the water. Jones and Bingham[2] have shown that the molecular conductivity of an N/200 solution of potassium iodide in acetone is about the same as in pure water. As the fluidity of acetone is about $2\frac{1}{2}$ times that of water, the dissociating action of acetone would be of the order of 40 per cent that of water. The relative association factors of water and acetone would lead to the same conclusion. While this conclusion may not be quantitatively accurate, it is safe to say that acetone is a strong dissociating agent. It is therefore possible that $\overline{OH}$ ions are split off from the glycerol by the combined action of the water and acetone, and possibly some from the water. This dissociation would explain the very high specific conductivities of the solvents used in this investigation as compared with those calculated by averaging the specific conductivities of the constituents.

[1]Carnegie Inst. Wash. Pub. No. 180. [2]*Ibid.*, No. 80.

Jones and Lindsay,[1] continuing the investigation of the phenomenon of minima in conductivity curves observed by Zelinsky and Krapiwin and by Cohen, advanced the theory, based on the hypothesis of Dutoit and Aston, that the decrease in conductivity and fluidity in solvents consisting of mixtures of associated liquids, was due to the fact that each liquid decreased the association of the other, thus decreasing the size of the ultimate unit particles composing the solvent and increasing the amount of frictional surface between them. With these two conceptions in mind; *i. e.*, the decrease in association of one associated liquid by another and the subsequent effect of the size of the particles; it seems clear that by the addition of a third associated liquid to such a binary mixture, the decrease in association would be carried farther, resulting in an increased amount of frictional surface and decreased fluidity. If the unit particles in the acetone were much larger than those already in the binary mixture, the fluidity of the resulting ternary mixture would be increased. This is not probable, as acetone is an associated liquid and the presence of three such liquids, each decreasing the association of the others, would, it is reasonable to conclude, result in a large increase in the number of smaller particles. All conductivity and fluidity measurements taken during this investigation support this view. The comparisons named below furnish some of the evidence for these conclusions.

To compare the results obtained with those calculated from averages, consider the data obtained by Davis and Jones with glycerol-water mixtures and by Davis, Hughes, and Jones with acetone-water mixtures. They used rubidium bromide in the following solvents: 75 p. ct. glycerol and 25 p. ct. water (A); 75 p. ct. acetone and 25 p. ct. water (B); 50 p. ct. glycerol and 50 p. ct. water (C); 50 p. ct. acetone and 50 p. ct. water (D).

It should be noted that the action of all four salts used in this investigation do not differ widely in the same solvents. The average obtained with the 2–1–1 and 1–2–1 solvents can be compared with the A and B solvents, since all contain 25 per cent water. The 75 per cent of ternary mixture is, by averaging the 1–2–1 and 2–1–1 solvents, equally divided between glycerol and acetone. Solvents C and D can be compared with the 1–1–2 solvents, since all contain 50 per cent water.

The fluidity of the 1–1–1 solvent is about one-sixth that calculated from averages; while the specific conductivity is, as noted above, about 3,000 times that calculated by the same method; hence the specific conductivity of the solvent is 18,000 times that which would be expected. While these figures can be considered only as a very rough approximation, they indicate a relatively large dissociation in these ternary mixtures.

[1]Carnegie Inst. Wash. Pub. No. 80.

Further evidence for this view is obtained from the 1–2–2 solvent, whose specific conductivity exceeds by a much larger amount that calculated by the method indicated above. The relative amounts of acetone and water are much larger in the 1–2–2 solvent than in the 1–1–1; hence a larger dissociation of the glycerol would be expected from the law of mass action.

The viscosity and fluidity tables are arranged in groups under each of the solvents. Thus, table 34 contains the data for rubidium bromide, rubidium iodide, and ammonium iodide in the 1–2–2 solvent. A similar arrangement is carried out for each of the seven solvents. Associated with each table of viscosities is a corresponding table of temperature coefficients, calculated by means of the formula given on page 122.

It has been shown that negative viscosity coefficients occur in all cases of rubidium salts in glycerol-water mixtures, and also for ammonium bromide and iodide in these solvents. Such was also found to be true in acetone-water mixtures, wherever the percentage of water was higher than that of acetone.

In the present investigation it appears that a similar behavior of such salts manifests itself wherever the solvents are of the same general nature as those mentioned above. Thus, negative viscosity coefficients are to be observed in the case of all the salts studied in the 1–1–1, the 2–1–2, and the 2–1–1 solvents. Here it is evident that either glycerol or water, or both, are present in greater proportions than acetone. Since glycerol is a solvent closely allied to water in its properties, we may disregard its enormous viscosity and compare these solvents with those acetone-water mixtures in which the water is present in the larger proportion; these solvents would then correspond to 25, 20, and 25 per cent acetone-water mixtures, in so far as the acetone affects the tendency of the salts to lower the viscosity of the solvent; while at the same time, because of their glycerol content, they have viscosity coefficients comparable with 50 to 25 per cent glycerol-water mixtures.

On the other hand, we have those solvents in which the percentage content of acetone exceeds either of the other two separately. Under this head are included the 1–2–1 solvent and, in certain instances, the solutions in the 2–2–1 mixture.

In the case of the 1–2–2 and the 1–1–1 solvents an apparent fluctuation is to be noted in the concentration curve for the various salts. Thus, the more concentrated solutions increase the viscosity of the solvent, while the more dilute lower it; a possible explanation of this phenomenon is suggested later in discussing the conductivity data. While this does not hold for all temperatures, it appears to be common to all the salts studied.

Tables 41 to 47 show the molecular conductivity, temperature coefficients in conductivity units, and percentages of ammonium iodide,

ammonium bromide, rubidium iodide, and rubidium bromide in each of the solvents. Figure 53 shows the conductivity curves of ammonium iodide in the ternary solvents at 25 degrees, and figure 54 shows the corresponding fluidity curves. While these curves have the same general character, some marked differences are noticeable. The fluidities of glycerol, water, and acetone at 25 degrees are respectively 0.17, 112.30, and 288.95. The values for glycerol and water are taken from the data of Jones and Davis and those for acetone from the work of Jones and Bingham. A study of these two figures in the light of the Thompson[1]-Nernst[2], and Dutoit-Aston[3] hypotheses will afford an explanation of all cases of non-parallelism in the two sets of curves. Since reducing the association of the solvent affects both its fluidity and dissociation, and since the relative effect on each is not known, the above explanation is to be regarded as only qualitative.

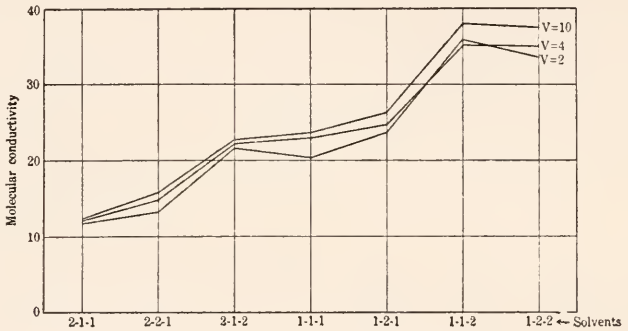


FIG. 53.—Conductivity of ammonium iodide in glycerol, acetone, and water, at 25°.

As an illustration, consider the change from the 1-1-1 solvent to the 1-2-1. The fluidity increases 5 times as much as the conductivity. The changes affecting fluidity are as follows: the water changes from 33 to 25 per cent causing a small reduction; glycerol changes from 33 to 25 per cent causing a rather large increase, while acetone changes from 33 to 50 per cent, causing a very large increase. The changes in water and glycerol would each reduce the conductivity, while the change in acetone would increase the conductivity much less than the fluidity. A consideration of the above details makes it clear that a much larger increase in fluidity than in conductivity should be expected.

Other changes from one solvent to another can be explained by similar considerations. Thus, figures 55 and 56 show fluidity and molecular conductivity curves for rubidium bromide in the 1-2-1 and the 1-1-2 solvents at 15°, 25°, and 35°. Jones, Davis, and Hughes have shown that for glycerol-water mixtures and acetone-water mixtures, temperature coefficients for fluidity are larger than for conductivity, because rising temperature decreases the dissociation.

[1]Phil. Mag., **36**, 320. (1893.) [2]Zeit. phys Chem., **13**, 531. (1894.)
[3]Compt. Rend., **125**, 240. (1897.)

These curves show that the same relation is true for the ternary solvents. Sufficiently dilute solutions have not been used in this work to determine the dissociation accurately, no measurements beyond N/800 having been made. The data obtained by Jones and Bingham, and the work on glycerol-water and acetone-water mixtures indicate that solutions more dilute than N/1600 must be used. Decrease in dissociation from 15° to 35° is slight, and is not sufficient to explain the difference between the fluidity and conductivity coefficients. Rubidium and ammonium salts are not in the class of salts that form complex solvates, yet of the known factors which affect conductivity the formation of solvates is the only one which can explain the point here raised. If a solvate is formed and the rise in temperature reduces its complexity less than it increases the fluidity of the solvent, the above is a satisfactory explanation. In this connection it should be noted that Jones and Guy[1] have found some evidence for the formation

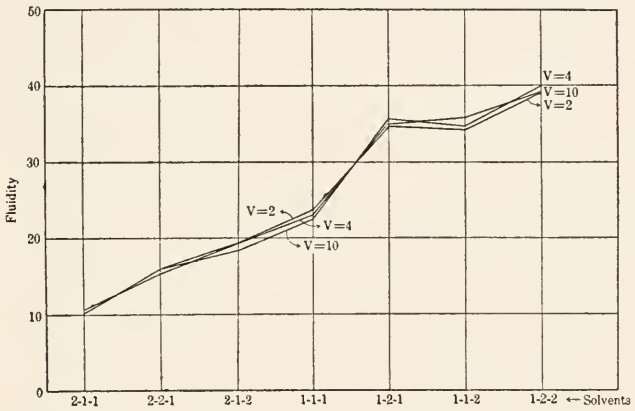


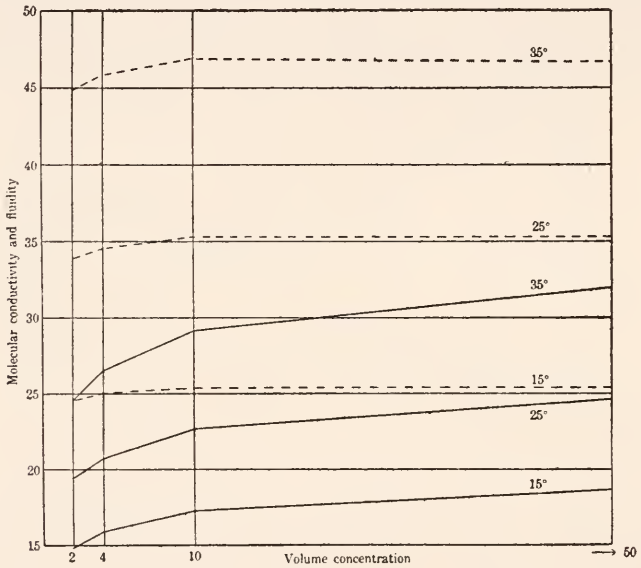
FIG. 54.—Fluidity of ammonium iodide in glycerol, acetone, and water, at 25°.

of glycerolates by sodium and potassium salts. The acetone-water investigation shows some evidence for the formation of solvates by rubidium salts in a mixed solvent. Another factor which should be investigated is the polymerizing action of acetone and the effect of temperature on the complexity of the polymers.

It should be noted that figures 55 and 56 show two distinct types of curves. In figure 55 both conductivity and fluidity curves are regular, while in figure 56 both curves show a minimum. The minimum occurs at the N/4 point. The effect on conductivity of the usual increase in dissociation from N/2 to N/4 is overcome by the decrease in fluidity, thus producing the minimum point. From N/4 to N/10 there is little change in fluidity, hence the increase in dissociation gives the curves a sharp upward turn. In figure 55 the influence of increasing fluidity and dissociation work together, producing a convex curve.

[1]Carnegie Inst. Wash. Pub. No. 180.

Returning to the fundamental point; why do these rubidium and ammonium salts cause conductivity minima and also fluidity minima in some of these ternary solvents and not in others? In some cases, a flat curve or a straight line is produced. In all such cases the fluidity coefficients are negative. These negative coefficients occur only with the solvents containing 40 and 50 per cent acetone. The first suggestion would be that it was due to some specific effect of acetone on the fluidities of these solvents, but a study of them and also of figure 58 renders this view open to question. The explanation suggested is the polymerizing action of acetone. The normal action of these salts is to produce positive fluidity coefficients on account of large molecular volumes. The formation of a polymer would reduce the number of



———— =conductivity curves. – – – – – – – – =fluidity curves.

FIG. 55.—Conductivity and fluidity of rubidium bromide in the 1–2–1 solvent at 15°, 25°, and 35°.

molecules and hence diminish or overcome the action that results in these positive coefficients. Jones and Mahin[1] have shown that cadmium iodide, lithium nitrate, and lithium acetate polymerize in acetone. More data on the polymerization of inorganic salts is desirable.

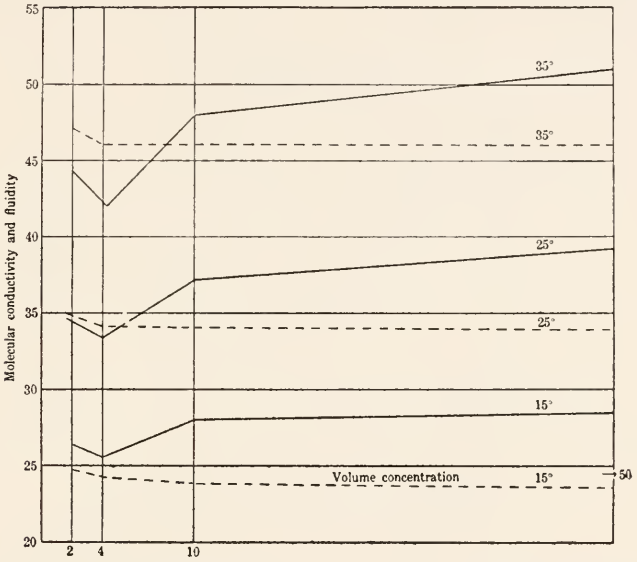
Figure 57 shows for comparison the temperature coefficients of conductivity and fluidity for an N/10 solution of ammonium iodide in the ternary solvents at 15° to 25° and 25° to 35°. There is a striking similarity between the curves for the conductivity and fluidity coefficients.[2] They are lower for the higher range in temperature, as

[1]Carnegie Inst. Wash. Pub. No. 180.

[2]The unusual feature shown by curve II for the 2–2–1 solvent is probably due to this solvent containing 40 per cent of acetone, a very volatile liquid. This solvent also contains only 20 per cent of water, which is the minimum amount necessary to cause these three liquids to form a homogeneous mixture.

would be expected from the work in other solvents. The temperature coefficients of conductivity are very close to those calculated from averages from the data of the glycerol-water and acetone-water investigations. As glycerol has a much higher temperature coefficient of conductivity than either acetone or water, the solvents containing the largest percentage of glycerol should have the highest coefficients. The curves are in keeping with this fact.

Conductivity and fluidity in these ternary solvents is much below the average. These considerations emphasize the fact that fluidity outweighs all the other factors that affect conductivity. Furthermore, as already noted, the fluidity data indicate that association is more



——— = conductivity curves. – – – – – – – – = fluidity curves.

FIG. 56.—Conductivity and fluidity of rubidium bromide in the 1–1–2 solvent at 5°, 25°, and 35°.

reduced in the ternary than in the binary solvents, but a decreased dissociation is not indicated, as might be expected from the deduction of Jones and Lindsay.

It is important to determine what effect glycerol, acetone, and water have on each other when constituting a ternary mixture. This investigation has shown that the properties of these ternary solvents are widely different from those which can be calculated from averages. The curves of figure 58 are drawn to show the differences between the measured and calculated conductivities and fluidities. To illustrate: the fluidity of the 2-1-1 solvent is 10.31 at 25°; calculated from averages it is 100.4; the measured is thus 10 per cent of the calculated; hence 10 is the ordinate for the 2-1-1 point. The data for drawing the con-

ductivity curves are not as full as could be desired. For acetone the value is taken from the data of Jones and Bingham[1] on potassium iodide for a N/200 solution at 25°. The data for rubidium bromide in glycerol and in water are taken from the work of Jones and Davis.[2] The action of potassium and rubidium salts in relation to conductivity are similar enough for the purpose of this comparison. The 2-1-1 ordinate shows that the measured conductivity is 19.2 per cent of the calculated. That the curves have the same character is another evidence for the close relation existing between conductivity and fluidity.

In figure 58 the solvents are arranged from left to right in the order of the percentage of glycerol which they contain; hence the curves show that the more glycerol the solvents contain, the more the con-

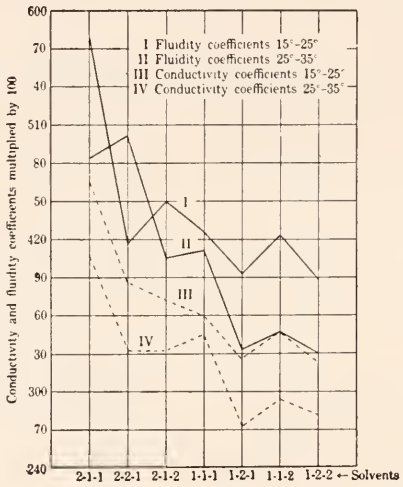


FIG. 57.—Conductivity and fluidity temperature coefficients for N/10 solution of ammonium iodide in glycerol, acetone, and water.

ductivity and fluidity values depart from the calculated averages. The theory of Jones and Veazey states that viscosity is due to the friction between the particles of the liquid. It is clear that the smaller the particles the greater will be the amount of frictional surface between them; hence, the greater the viscosity of any homogeneous liquid, the smaller must be the particles composing it. The density of the liquid should also affect the viscosity. The densities of glycerol, water, and acetone are 1.26, 1.00 and 0.79, respectively, while the fluidities are in the ratio 1 : 702 : 1741; hence the variation in density is so small in comparison with the variation in fluidity that the former can be neglected. It seems probable that there is one other important factor that affects fluidity, which must be considered in addition to the size of the particle. The particle in a pure homogeneous liquid would be either one molecule or an association of molecules.

[1]Carnegie Inst. Wash. Pub. No. 80. [2]*Ibid.*, No. 180.

The conception of molecular volume is opposed to the view that the glycerol particle is smaller than that of acetone or water. Acetone and glycerol have the same molecular volume, calculated on the basis of the simple molecule, *i. e.*, 73; water has 18. Considering the association factors, the molecular values are as follows: glycerol 150, acetone 92, water 72. From the latter consideration, glycerol has the larger molecular volume, and hence should have the highest fluidity, which is contrary to the facts. The error probably arises from the use of the density factor in calculating molecular volume. The density of a liquid is affected by both the density of the molecules and the spaces between them. The kinetic molecular hypothesis states that for a gas the space between the molecules is much greater than that occupied by the molecules. For a liquid, the intermolecular space is less than for a gas, and for a solid less than for a liquid. For liquids it seems

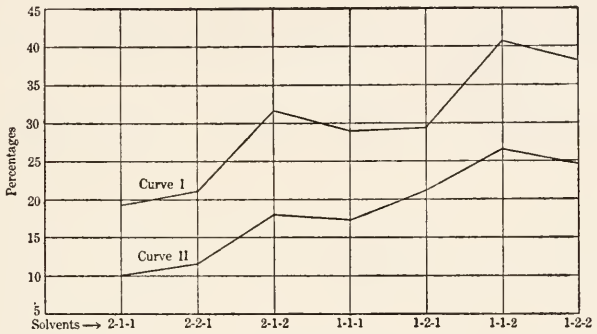


FIG. 58.—Ordinates are percentages by which measured conductivity and fluidity differ from the values calculated by averages.

Curve I, calculated from conductivity of RbI at 25°.
Curve II, calculated from fluidity of solvents at 25°.

reasonable to believe that the density of the liquid gives no idea of the density of the molecule or the space between them; and it is the latter factor of intermolecular space as well as the size of the particle that must be considered as the chief factor governing fluidity. Hence the conception of molecular volume as applied to liquids is not opposed to the theory that fluidity depends on the frictional surface between the particles or molecular associations, and the necessary corollary that the amount of frictional surface depends on the size of the particles. It should be noted in this connection that it is clear that the intermolecular space of a gas is the most important factor affecting its viscosity. It is reasonable to believe that the same factor must be considered in studying the viscosity or fluidity of liquids, although it is relatively less important than for gases. It is probable that the present conception of molecular volume as applied to solids is approximately correct, since the intermolecular space may be so small that it can be neglected.

SUMMARY.

1. The conductivities of the ternary solvents make it probable that water and acetone act as dissociating agents on glycerol.

2. The decrease in dissociation of one associated liquid by another is much larger in a ternary than in a binary mixture, thus producing decreased values in conductivity and fluidity.

3. A consideration of the hypotheses of Dutoit and Aston and of Thompson-Nernst, together with the fluidities of glycerol, acetone, and water, explain the differences between the conductivity and fluidity curves in these ternary solvents.

4. Temperature coefficients of fluidity are larger than for conductivity, as in binary solvents. The formation of solvates is a possible explanation of the difference between these coefficients.

5. The minimum point which occurs in some of the conductivity curves is explained by considering the fluidity of the solution.

6. A possible explanation of the fluidity changes which produce minima in the conductivity and fluidity curves is the polymerization of the salts by the acetone.

7. The conductivity and fluidity values of the solvents containing the largest percentage of glycerol are farthest below the values calculated by averages.

8. The temperature coefficients of conductivity are about the same as those calculated from averages.

9. This investigation emphasizes the fact already known that fluidity probably outweighs all the other factors affecting conductivity.

10. The conditions governing viscosity in a pure homogeneous liquid are discussed from a physical point of view.

CHAPTER VII.

DISCUSSION OF EVIDENCE ON THE SOLVATE THEORY OF SOLUTION OBTAINED IN THE LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY.[1]

About fifteen years ago the work which led to the present theory of solution was begun in this laboratory. From a very simple beginning, which did not have for its object the study of the nature of solution in general, the work has widened in a fairly large number of directions. There have already been published by my co-workers and myself about eighty papers dealing with one or another phase of the problem. These are fairly widely scattered through chemical and physical literature, having been published in American, German, French, and English scientific journals. In addition, the Carnegie Institution of Washington, which has so generously supported the work, and without which it would have been impossible to have carried out many of the investigations, has published nine monographs of researches bearing directly and indirectly on the question of the nature of solution.

Taking all of these facts into account, it has seemed desirable to discuss here, as briefly as possible, the more important lines of evidence which have been brought out, bearing on the nature of that condition of matter which gives rise to the sciences of chemistry, geology, and to a large part of biology.

EARLIER WORK.

In the summer of 1893 I went to Stockholm to work with Svante Arrhenius. He suggested that we carry out a research on the question as to whether sulphuric acid forms a few definite hydrates when in the presence of water, as the theory of Mendeléeff maintained. According to this theory, some of these hydrates were very complex, one of them containing as much as 100 molecules of water to 1 molecule of sulphuric acid. Mendeléeff arrived at this conclusion chiefly from a study of the specific gravities of aqueous solutions of sulphuric acid of different concentrations. The specific-gravity curves showed certain discontinuities or breaks, which Mendeléeff interpreted to mean the existence of definite chemical compounds or hydrates.

At the suggestion of Arrhenius, I studied the problem in the following way. Acetic acid was used as the solvent. The freezing-point lowerings of the acid produced by adding different known amounts of water were determined. The freezing-point lowerings produced by adding known amounts of sulphuric acid to pure acetic acid were measured. The freezing-point lowerings produced by adding, simultaneously, known amounts of sulphuric acid and known amounts of water to known

[1]See paper in Journ. Franklin Institute, Nov. and Dec. 1913.

amounts of acetic acid were also determined. By comparing the three sets of results, from Raoult's law we could calculate the composition of the hydrates formed by the sulphuric acid, if any were formed.

We added large amounts of water relative to the sulphuric acid, but could obtain no evidence of any hydrate of sulphuric acid more complex than $H_2SO_4,2H_2O$, which is the well-known compound H_6SO_6. We did not obtain the slightest evidence of the existence of any of the more complex hydrates which Mendeléeff, from his work, had supposed to exist. I was, therefore, at that time, thoroughly convinced of the untenability of the Mendeléeff theory of hydrates, and, indeed, of any theory of hydration. I regarded the ions in solution as having an existence not only independent of one another, but also independent of the molecules of the solvent. In a word, I was at that time firmly convinced that no theory of hydration was necessary to explain the facts that were then known. This seemed to be the view which was held at that time also by most of those who founded the new school of chemistry.

A comparatively few years later, my cooperators, Ota[1] and Knight,[2] brought to light certain facts which could not be explained in terms of any relation that was then known. They found that certain double salts, such as double chlorides, nitrates, sulphates, cyanides, etc., produced abnormally great lowering of the freezing-point of water when the solutions were concentrated. What was more perplexing was the fact that the *molecular depression of the freezing-point increased with the concentration* beyond a certain definite concentration.

Similar results were found for a fairly large number of salts by Jones and Chambers,[3] and by Chambers and Frazer working with Jones.[4] The salts studied by these workers were those that are known to be very hydroscopic, to have great power of combining with water. The question arose, what did these results mean? At that time I was antagonistic to any hydrate theory. My experience in the laboratory of Arrhenius had produced that state of mind; yet I was unable to explain our results in terms of any other assumption than that a part of the water present was combined with the dissolved substance, and was therefore removed from playing the role of solvent. I ventured this suggestion, for want of any better in 1900.[5]

The suggestion of hydration in aqueous solution would explain the results that had been obtained. If a part of the water present was combined with the dissolved substance, there would be less water acting as solvent; and since freezing-point lowering is proportional to the ratio between the number of molecules of the solvent and of the dissolved substance, the less solvent present the greater the lowering of its freezing-point. It is one thing to make a suggestion which accounts for the known facts; it is a very different matter to show that this is

[1] Amer. Chem. Journ., **22**, 5 (1899).
[2] *Ibid.*, 110 (1899).
[3] *Ibid.*, **23**, 89 (1900).
[4] *Ibid.*, 512 (1900).
[5] *Ibid.*, **23**, 103 (1900).

the only reasonable suggestion which will account for them, to show that the suggestion is true.

Aided by a grant from the Carnegie Institution of Washington, I started Dr. Getman[1] on a more or less systematic study of the whole problem. The question arose, were the results already obtained limited to a few compounds, or types of compounds, or was this a general phenomenon? We took up the study of acids, bases, and salts in concentrated solutions, especially by the freezing-point and conductivity methods. We also studied the refractivities of many solutions.

RELATION BETWEEN LOWERING OF THE FREEZING-POINT OF WATER AND WATER OF CRYSTALLIZATION OF THE DISSOLVED SUBSTANCE.

The work of Getman included the study of the lowering of the freezing-point of water produced by concentrated solutions of the chlorides of sodium, potassium, ammonium, lithium, barium, strontium, calcium, magnesium, iron, and aluminium; the bromides of sodium, potassium, lithium, barium, strontium, calcium, magnesium, and cadmium; the iodides of sodium, potassium, lithium, calcium, barium, strontium, and cadmium; and the nitrates of sodium, potassium, ammonium, lithium, calcium, magnesium, manganese, cobalt, nickel, cadmium, zinc, aluminium, iron, and chromium. The relation between lowering of freezing-point and water of crystallization can be seen very well from the curves.[2]

The nitrates of sodium, potassium, and ammonium, which crystallize without water, produce the smallest lowering of the freezing-point of water. Then come the nitrate of lithium with 2 molecules of water, calcium with 4, and a large number of nitrates each with 6 molecules of crystal water; all give about the same lowering of the freezing-point. Finally, the three nitrates of aluminium, iron, and chromium with 8 and 9 molecules of water, give the greatest lowering of the freezing-point of water.

Relations similar to the above come out for the chlorides, the bromides, and the iodides.[3] The freezing-point lowerings of water produced by them are roughly proportional to the amounts of water with which the salts crystallize.

If, on the other hand, we compare the chlorides with the bromides, with the iodides, with the nitrates, similar relations manifest themselves.

It was found that chlorides, bromides, iodides, and nitrates which have no water of crystallization, all produce about the same molecular lowering of the freezing-point of water, and this is between 3 and 4.

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[1]Amer. Chem. Journ., **27**, 433 (1902); **31**, 303 (1904); **32**, 308 (1904); Zeit. phys. Chem., **46**, 244 (1903); **49**, 385 (1904); Phys. Rev., **18**, 146 (1904); Ber. d. chem. Gesell., **37**, 1511 (1904).

[2]See Carnegie Inst. Wash. Pub. No. 60, p. 24.

[3]See Carnegie Inst. Wash. Pub. No. 60, pp. 20–26.

With salts that crystallize without water there is only a very slight increase in the molecular lowering of the freezing-point with increase in the concentration of the solution. The salts of lithium, which crystallize with the same amounts of water, give approximately the same depressions of the freezing-point.

If we compare the salts of the alkaline earths that crystallize with 6 molecules of water, they produce approximately the same lowerings; the nitrates of iron and aluminium with 8 and 9 molecules of water give greater lowerings than the corresponding halogens with 6.

In the first case we have kept the acid constant and compared with one another the salts of the different metals with the same acid. In the second case we have kept the metal constant, and compared the salts of a given metal with different acids. In both cases the relation between lowering of the freezing-point of water by the dissolved substance and water of crystallization of the dissolved substance manifests itself.

These salts that crystallize with the largest amounts of water produce the greatest molecular lowering of the freezing-point of water. The work was done with concentrated solutions, and it has already been pointed out that for such substances the molecular lowering of the freezing-point increases with the concentration of the solution.

We must now ask what bearing has this relation on the question of hydration or non-hydration in aqueous solution? A moment's thought will show that the bearing is a very direct one. If hydrates exist in aqueous solution, those substances which in such solutions would form the most complex hydrates would be the substances that would crystallize from aqueous solutions with the largest amounts of water. This is the same as to say that those substances which, in the presence of a large amount of water, have the greatest power to combine with water, would, other things being equal, be the ones to bring with them, out of aqueous solution, the largest amounts of water as water of crystallization.

We could not, however, expect one of these phenomena to be strictly a linear function of the other, since there are undoubtedly other factors, such as shape of molecules, angles of crystals, etc., coming into play in determining the exact composition of crystals.

That a relation such as was pointed out above holds so well and so generally for such a large number of substances is very significant and early led me to believe that the suggestion of hydration in general in aqueous solution contained more truth than I imagined when it was first suggested.

Having found a relation such as the above, we were led to look about for others that would bear directly or indirectly on the problem in hand. Before taking up these, another feature of the work of Getman must be briefly discussed.

APPROXIMATE COMPOSITION OF THE HYDRATES FORMED BY VARIOUS SUBSTANCES IN SOLUTION.

The line of evidence just discussed seemed so strongly in favor of the general correctness of the view that there is combination between the dissolved substance and some of the water present, that Jones and Getman[1] undertook to calculate the approximate composition of the hydrates formed by the different substances, and by the same substance at different dilutions.

The experimental work consisted in determining the freezing-point of the solution and, consequently, the depression of the freezing-point of water produced by the dissolved substance at the concentration in question. From the freezing-point lowering the molecular lowering was calculated.

The dissociation of the solution was measured by means of the conductivity method. Knowing the dissociation, the theoretical molecular lowering was calculated on the assumption that none of the solvent was combined with the dissolved substance. The ratio of the theoretical molecular lowering to the value found experimentally, gave the proportion of all the water present that was uncombined. The remainder of the water was, of course, combined with the dissolved substance. The total amount of water present in any given solution could be readily determined. It was only necessary to take the specific gravity of the solution by weighing a known volume of it. Knowing the specific gravity and the concentration, it was, of course, perfectly simple to determine the total amount of water in, say, a liter of the solution. The total amount of water in the solution and the percentage of combined water being known, the total amount of combined water was known. Knowing the amount of dissolved substance present in, say, a liter of the solution, and knowing the total amount of water combined with it, it was perfectly simple, from the molecular weights of the dissolved substance and the solvent, to calculate how many molecules of water were combined with one molecule of the dissolved substance. The results of such a calculation are only approximations. In the first place, the conductivity method of measuring dissociation is not accurate for concentrated solutions, and there is no thoroughly accurate method known for this purpose. The error here is, however, in all probability not very large. Another source of error, which is probably larger, results from the assumption that Raoult's law holds for concentrated solutions, *i. e.*, that for concentrated solutions the lowering of the freezing-point is proportional to the concentration. This is not strictly the case, and we do not know at present how wide the deviation from Raoult's law is in concentrated solutions.

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[1]Carnegie Inst. Wash. Pub. No. 60.

Taking all of these factors into account, it still seems highly probable that, by the method outlined above, we can arrive at a reasonably close approximation to the amount of water combined with a molecule, or the resulting ions, of a dissolved substance, under given conditions of concentration. Whatever objection may be offered to this method of calculating the approximate composition of the hydrates existing in aqueous solution, it should be stated that it is the only general method thus far worked out for throwing any light whatever on this important problem. Jones and Getman applied this method of calculating the approximate composition of hydrates to about 100 compounds—salts, acids, and organic substances—and to about 1,500 solutions of these substances. Their results have been recorded in Publication No. 60 of the Carnegie Institution of Washington.

Salts of lithium form more complex hydrates than those of sodium and potassium. This would be expected, since lithium salts crystallize with water, while the salts of the other alkalies in general crystallize without water.

Salts of potassium and ammonium generally crystallize without water, and these compounds, as would be expected, combine with relatively little water in aqueous solution.

Many salts of sodium crystallize without water, and these hydrate very slightly. Other sodium salts, such as the bromide and iodide, crystallize with water and show considerable hydrating power in solution.

Salts of calcium crystallize with water and all have, as would be expected, large hydrating power. The halogen salts crystallize with 6, the nitrate with 4 molecules of water. The nitrate was found to have less hydrating power than the chloride or bromide.

The salts of strontium resemble those of calcium, both in the amounts of water with which they crystallize and with which they combine in aqueous solution. Salts of barium crystallize with less water and show less hydration than those of calcium and strontium.

The salts of magnesium have just about the hydration that would be expected from their water of crystallization. The same may be said of the salt of zinc that was studied.

Cadmium is of special interest. Its halogen compounds crystallize with little or no water, and although cadmium belongs in the same group with metals of large hydrating power, its halogens combine with only a small amount of water. The nitrate of cadmium crystallizes with 4 molecules of water and, as could be predicted, shows considerable hydrating power.

The chloride and nitrate of magnesium show the hydration that would be expected from their water of crystallization. The same may be said of the salts of nickel, cobalt, and copper.

The chlorides and nitrates of aluminium, iron, and chromium crystallize with large amounts of water and show great hydrating power.

The strong mineral acids show some hydrating power, but the complexity of the hydrate formed by these substances seems to pass through a maximum. The acids thus differ from the salts.

Some 13 non-electrolytes were studied as to their hydration, and none of them showed any appreciable hydration. The same applies to the organic acids that were studied in this connection.

The following general relations were brought out by the work of Jones and Getman. The total amount of water held in combination by the dissolved substance increases as the concentration of the solution increases. From what is known of mass action, this would be expected.

The number of molecules of water combined with 1 molecule of the dissolved substance generally increases from the most concentrated to the most dilute solution studied. In some cases, however, the number of molecules of combined water seems to pass through a maximum. These results, we believe, give us the approximate amounts of combined water, and certainly the relative hydrating powers of the different compounds with which we worked.

One other relation bearing on the question of hydration in aqueous solution was brought out by the work of Jones and Getman.

RELATION BETWEEN THE MINIMA IN THE FREEZING-POINT CURVES AND THE MINIMA IN THE BOILING-POINT CURVES.

It has already been pointed out that if we plot the molecular lowerings of the freezing-point as ordinates against the concentrations of the solutions as abscissæ, the curves have a well-defined minimum; from this minimum they rise both with dilution and with concentration. What is the meaning of this minimum? The curves rise with dilution because of increasing dissociation; they rise with increasing concentration because the total amount of combined water increases with the concentration of the solution; and consequently the lowering of the freezing-point of the ever-decreasing amount of solvent water becomes greater and greater. The minima in freezing-point curves are, then, the points where the two opposite effects increase in dissociation with dilution and increase in combined water with concentration, just offset one another.

The rise in the boiling-points of solvents produced by dissolved substances was also studied, and at different concentrations. Boiling-point curves were plotted analogous to the freezing-point curves; *i. e.*, molecular rise in the boiling-point as ordinates and concentrations as abscissæ. These curves also had minima, and we interpreted the minima here in a manner analogous to our interpretation of the minima in the freezing-point curves—they are the points of equilibrium between increasing dissociation with dilution, and increasing hydration with concentration.

A comparison of the freezing-point with the boiling-point curves brought out a relation of interest, and we believe of some importance in the present connection. The minima in the boiling-point curves

occur at greater concentration than in the freezing-point curves. What is the meaning of this relation? To see this we must first call attention to one property of hydrates which has thus far not been referred to. They are very unstable, and readily break down with rise in temperature. This is easily seen if we consider the facts in the case of a salt like calcium chloride. At ordinary temperatures there may be as much as 30 molecules of water combined with 1 molecule of the salt; while at the boiling-point of the saturated solution all of the water can be removed except the 6 molecules with which the salt crystallizes. The higher the temperature to which a solution is heated the less the hydration in such a solution. Solutions, of course, boil higher than they freeze. There is therefore less hydration in the boiling than in the freezing solution. Consequently, to produce enough hydration to give the minimum in the curve would require a greater concentration of the solution at its boiling-point than at its freezing-point.

The fact is, then, not only in accord with the hydrate conception, but could readily have been predicted from it, as a necessary consequence of the theory.

RELATION BETWEEN WATER OF CRYSTALLIZATION AND TEMPERATURE OF CRYSTALLIZATION.

Jones and Bassett[1] worked out the approximate composition of the hydrates formed by a large number of substances, and also the following relation. The hydrates, as we have seen, are very unstable systems. They are readily broken down in solution with rise in temperature. The hydrates which exist in solution at ordinary temperatures are much more complex than those which the salts can bring with them out of solution as water of crystallization. The hydrates are more stable and more complex the lower the temperatures. We were, however, surprised, on examining the literature, to find the large number of examples on record of salts crystallizing with varying amounts of water, depending on the temperature at which the crystals were formed.

A few examples will be given to bring out the general relation that the number of molecules of water of crystallization is larger the lower the temperature at which the salt crystallizes.

$CaCl_2$	H_2O, $2\ H_2O$, $4\ H_2O$, $6\ H_2O$	As the temperature of crystallization is lower and lower.
$MnCl_2$	$2\ H_2O$	20°.
	$4\ H_2O$	15°.
	$6\ H_2O$	−21°.
	$11\ H_2O$	−21° to −37°.
	$12\ H_2O$	−48°.
$FeCl_3$	anhydrous	80° and above.
	$2\ H_2O$	60° to 80°.
	$2\frac{1}{2}\ H_2O$	40° to 60°.
$MgCl_2$	$6\ H_2O$, $8\ H_2O$	Elevated temperatures above 20°.
	$10\ H_2O$	20°.
	$12\ H_2O$	−10° to −12°.
$MnSO_4$	$3\ H_2O$	25° to 31°, as a
	$4\ H_2O$	25° to 31°.
	$5\ H_2O$	15° to 20°.
	$7\ H_2O$	0° or below 0°.
$FeCl_3$	$3\frac{1}{2}\ H_2O$	20°.
	$6\ H_2O$	20° to −16°.

[1]Carnegie Inst. Wash. Pub. No. 60. Amer. Chem. Journ., **33**, 534 (1905); **34**, 291 (1905). Zeit. phys. Chem., **52**, 231 (1905).

These examples suffice to show the general nature of the relation between water of crystallization and the temperature at which the salt crystallizes. This relation could have been foreseen as a necessary consequence of the theory of hydrates in aqueous solution, and the instability, with temperature, of those hydrates.

HYDRATE THEORY IN AQUEOUS SOLUTIONS BECOMES THE SOLVATE THEORY IN SOLUTIONS IN GENERAL.

The earliest work on the problem of the nature of solution was limited to water as the solvent. It was found that salts in general have the power to combine with more or less of the water in which they are dissolved—have a greater or less hydrating power. This power is, however, possessed to a very different degree by the different compounds. As we have seen, the degree of hydration of a salt can be approximately determined by the amount of water with which it crystallizes at ordinary temperatures.

It having been made probable that hydration exists in aqueous solution, the question arose, do dissolved substances have the power to combine with other solvents in which they are dissolved?

To test this Jones and Getman[1] studied, by the boiling-point method, solutions of lithium chloride and nitrate, and calcium nitrate in ethyl alcohol. They used also a number of other salts. It was found that the molecular rise in the boiling-point was not only greater than the theoretical rise at nearly all of the concentrations studied, but the molecular rise increases rapidly with the concentration of the solution. The molecular rise of the boiling-point of ethyl alcohol, produced by lithium chloride, increases from 1.28 at 0.07 normal to 2.43 at 2.07 normal. In calculating the theoretical molecular rise the dissociation is, of course, taken into account. The dissociation decreases with the concentration, which would tend to decrease the molecular rise in the boiling-point. Notwithstanding this influence, we have seen that the molecular rise in the boiling-point of solutions of certain salts in ethyl alcohol increases as the concentration of the solution increases.

The differences between the theoretical and the experimental results are in some cases quite large. Jones and Getman[2] interpreted these results in ethyl alcohol in a manner analogous to that which they had adopted in the case of aqueous solutions. The abnormally large rise in the boiling-point of ethyl alcohol, produced by certain salts, and the increase in the molecular rise of the boiling-point with increase in the concentration of the solution, are due to combination between the dissolved substance and part of the solvent—to the formation of ethyl alcoholates in solution. The part of the alcohol that is combined with the dissolved substance is thus removed from the field of action as far as solvent is concerned. There being less alcohol present acting

[1] Amer. Chem. Journ., **32**, 338 (1904). [2] *Ibid.*, 339 (1904).

as solvent, the rise in its boiling-point produced by a given amount of dissolved substance would be larger than if all the alcohol were playing the part of solvent.

Further, if the dissolved substance combines with a part of the alcohol, the more concentrated the solution the greater the total amount of alcohol held in combination. This would explain the increase in the molecular rise in the boiling-point with increase in the concentration of the solution. This suggestion of combination between a part of the solvent and the dissolved substance explains the facts in alcoholic solutions just as well as the hydrate theory explains the facts in aqueous solutions.

The work of Jones and Getman in solutions in ethyl alcohol as the solvent was extended by Jones and McMaster to methyl alcohol. They also extended the work in ethyl alcohol as the solvent. They repeated a part of the work of Jones and Getman in ethyl alcohol and obtained results of the same general character as had been found by the earlier workers.

They used the boiling-point method with methyl alcohol as the solvent, and the chloride, bromide, and nitrate of lithium as the dissolved salts. The molecular rise in the boiling-point, even in the most dilute solutions, was greater than could be accounted for by the dissociation. This is, of course, entirely incapable of accounting for the increase in the molecular rise with increase in the concentration of the solution, which manifests itself in the case of every salt studied in this solvent, dissociation decreasing with increase in concentration, which would tend to diminish the molecular rise in the boiling-point.

The magnitude of the molecular rise in the most concentrated solutions is very large indeed. It is almost twice the boiling-point constant, or normal molecular rise for this solvent; and the dissociation of such solutions is certainly not more than 25 to 30 per cent, and probably less than this value.

We interpreted these results as we did those in ethyl alcohol as the solvent—there is combination between a part of the alcohol present and the dissolved substance, forming methyl alcoholates. As the concentration increases, more and more alcohol is held in combination by the dissolved substance; consequently, there is an increase in the molecular rise of the boiling-point.

It thus seems that evidence was furnished of combination between methyl alcohol and the dissolved substance, on the one hand, and ethyl alcohol and the dissolved substance on the other. As we shall see later, evidence has been obtained of combination between acetone and substances dissolved in it; and other solvents have been and are being brought within the scope of this work.

In every case thus far investigated there seems to be good evidence in favor of the view that there is combination between the dissolved

substance and a part of the solvent present. In a word, combination of solvent with dissolved substance—solvation—seems to be a more or less general phenomenon. The original hydrate theory thus becomes the *solvate theory of solution.*

TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND HYDRATION.

A fairly elaborate investigation on the conductivities, dissociation, and temperature coefficients of conductivity and dissociation of aqueous solutions was begun in my laboratory about 15 years ago and is still in progress. The work, as a whole, has been recently published by the Carnegie Institution of Washington.[1] The monograph in question contains the investigations of Clover,[2] Hosford,[3] Howard,[4] Jacobson,[5] Kreider,[6] Shaeffer,[7] Smith,[8] Springer,[9] West,[10] Wight,[11] Wightman,[12] and Winston.[13] The results published in this monograph are for about 110 salts, which were studied from zero to 65°, and from the most concentrated solution that could be used to the dilution in most cases of complete dissociation. The temperature coefficients of conductivity were calculated both in conductivity units and in percentage.

Similar data were obtained for about 90 of the more common organic acids, and the constants for the weaker acids were calculated from the Ostwald dilution law. The dissociations of the salts and acids at the different temperatures were, whenever possible, also calculated.

The temperature coefficients of conductivity were calculated both in percentage and in conductivity units. A study of the temperature coefficients of conductivity, expressed in conductivity units, brought out a relation which had a very direct bearing on the question of hydration in aqueous solution. This is so important that it will be discussed here in some detail.

The conductivity of a solution is conditioned by the number of ions present and the velocities with which they move. Rise in temperature not only does not increase the number of ions present, but, as is well-known, diminishes dissociation. The effect of rise in temperature increasing the conductivity of solutions is, then, due to an increase in the velocities with which the ions move. If the ion is driven by a constant force, its velocity would be determined chiefly by the viscosity of the solvent and by the mass and size of the ion. With rise in temperature the driving force would be increased. Rise in temperature would also decrease the viscosity of the solvent. The effect of

[1] Carnegie Inst. Wash. Pub. No. 170.
[2] Amer. Chem. Journ., **43**, 187 (1910).
[3] *Ibid.*, **46**, 240 (1911).
[4] *Ibid.*, **48**, 500 (1912).
[5] *Ibid.*, **40**, 355 (1908).
[6] *Ibid.*, **45**, 282 (1911).
[7] *Ibid.*, **49**, 207 (1913).
[8] *Ibid.*, **50**, 1 (1913).
[9] *Ibid.*, **48**, 411 (1912).
[10] *Ibid.*, **44**, 508 (1910).
[11] *Ibid.*, **42**, 520 (1909); **44**, 159 (1910).
[12] *Ibid.*, **46**, 56 (1911); **48**, 320 (1912).
[13] *Ibid.*, **46**, 368 (1911).

rise in temperature on both of these factors would be to increase the velocities of the ions and, consequently, the conductivity.

Another factor must, however, be taken into account. That many ions in aqueous solutions are strongly hydrated seems now quite generally accepted. We have seen that these hydrates are relatively unstable and break down with rise in temperature. The simpler the hydrate formed by an ion, the smaller the mass of the ion; the smaller the mass of the ion, other things being equal, the less resistance it will offer when moving through the solvent. Therefore, rise in temperature should increase the velocity of the ion.

TABLE 48.—*Temperature coefficients of conductivity.*

Substances with slight hydrating power.	Temperature coefficients in conductivity units.			
	25° to 35°		50° to 65°	
	$v=8$	$v=1024$	$v=8$	$v=1024$
Sodium chloride	2.00	2.46	2.27	2.82
Sodium bromide	1.89	....	2.18	2.79
Sodium iodide	2.12	2.54	2.33	3.14
Sodium nitrate	2.04	2.45	2.02	2.67
Sodium chlorate	1.77	2.22	2.15	2.90
Potassium chloride	2.39	2.84	2.45	3.11
Potassium bromide	2.43	2.91	2.45	3.11
Potassium iodide	2.38	2.91	2.65	3.37
Potassium nitrate	2.08	2.16	2.31	2.83
Potassium chlorate	2.02	2.52	2.23	2.94
Potassium permanganate	2.04	2.31	2.29	2.23
Potassium sulphocyanate	2.20	2.56	2.34	....
Ammonium chloride	2.42	2.94	2.51	3.69
Ammonium bromide	2.32	2.86	2.58	3.11
Ammonium nitrate	2.17	2.50	2.33	3.04

If decreasing complexity of the hydrate formed by the ion with rise in temperature plays any prominent part in determining the large temperature coefficient of conductivity, since the complexity of such hydrates would decrease more with rise in temperature, we should expect to find that the ions which have the greatest hydrating power would have the largest temperature coefficients of conductivity. This is a concrete and, it would seem, necessary consequence of the hydrate theory in aqueous solutions. Further, it is one which can be tested directly by experiment. Is it true?

We have seen that the hydrating power of a salt, or the ions into which it dissociates, is approximately proportional to the number of molecules of water with which it crystallizes. This is the same as to say that the salt which has the greatest power to bring water with it out of solution is the one, other things being equal, which would hold the largest number of molecules of water in combination with it in solution. The question is, therefore, is there any relation between

the number of molecules of water with which a salt crystallizes and its temperature coefficients of conductivity?

This relation has already been discussed in Publication No. 170 of the Carnegie Institution of Washington, in which the results of our work on conductivity and dissociation has been published. Tables 48 and 49, showing temperature coefficients in conductivity units between the temperatures 25° and 35°, on the one hand, and between 50° and 65° on the other, at the dilutions $\frac{1}{8}$ and $\frac{1}{1024}$ normal, are taken from the monograph referred to above.

TABLE 49.—*Temperature coefficients of conductivity.*

Substances with large hydrating power.	Temperature coefficients in conductivity units.			
	25° to 35°		50° to 65°	
	$v=8$	$v=1024$	$v=8$	$v=1024$
Calcium chloride	3.49	4.85	....	....
Calcium bromide	3.73	5.00	4.03	6.03
Calcium nitrate	3.09	4.79	3.33	....
Strontium chloride	3.37	5.13	3.92	6.02
Strontium bromide	3.66	5.27	4.08	....
Strontium nitrate	2.76	4.86	3.58	....
Barium nitrate	3.09	4.74	3.34	....
Magnesium chloride	3.40	4.72	3.61	....
Magnesium bromide	3.55	4.44	4.08	....
Magnesium nitrate	3.10	4.78	3.57	....
Zinc nitrate	3.13	4.47	3.43	5.41
Manganous chloride	3.14	4.86	3.43	6.37
Nickel chloride	3.41	5.04	3.61	....
Nickel nitrate	3.21	4.58	....	....
Cobalt chloride	3.39	4.95	3.54	....
Cobalt bromide	3.32	4.96	3.75	....
Cobalt nitrate	3.20	4.67	3.05	....
Cupric nitrate	3.18	4.88	....	....
Aluminium chloride	4.57	8.64	5.16	12.49
Aluminium nitrate	4.19	7.86	4.87	11.65

We have seen that the hydrates formed by a large number of salts, including those given in tables 48 and 49, have already been worked out,[1] and that water of crystallization is a rough measure of water of hydration. The salts in table 48 crystallize with little or no water, and in aqueous solution are very little hydrated; those in table 49, in general, crystallize with large amounts of water and are strongly hydrated compounds.

Let us compare the temperature coefficients of conductivity in conductivity units (which are the actual increases in molecular conductivity per degree rise in temperature) of the substances in table 48 with those in table 49. It will be seen that the coefficients for the substances in table 48 are, at all dilutions and temperatures, much smaller

[1]Carnegie Inst. Wash. Pub. No. 60.

than those in table 49. In making this comparison we must, of course, take into account the fact that the substances in table 48 are binary electrolytes, each molecule breaking down into 2 ions, while the substances recorded in table 49 are all ternary electrolytes, each molecule breaking down into 3 ions, except the two salts of aluminium which are quaternary electrolytes, each molecule yielding 4 ions. Even taking all of these facts into account, the temperature coefficients of conductivity for the slightly hydrated salts are much smaller than those for the strongly hydrated compounds. This is exactly what would be expected. The complexity of the hydrates of slightly hydrated salts could change only a little with rise in temperature. Consequently, the mass of the hydrated ion would change only slightly with rise in temperature, and this effect of temperature on conductivity would be very small.

Another relation manifests itself when we compare the results in table 48 with one another, and those in table 49 with one another. If the temperature coefficient of conductivity is a function of the decreasing complexity of the hydrate formed by the ion, as the temperature is raised we should expect that those substances which have equal hydrating power would have approximately the same temperature coefficients of conductivity.

The substances in table 48 have only slight hydrating power, shown by the fact that they crystallize with little or no water. The fact is, their temperature coefficients of conductivity are all of the same order of magnitude.

The salts in table 49 have different hydrating power, but all have great power to combine with water in aqueous solution. A large number of these compounds have approximately the same hydrating power, as would be expected from the fact that many of them crystallize with 6 molecules of water. Barium chloride crystallizes with only 2 molecules of water, yet forms hydrates of complexity comparable with the other salts[1] in this table. Its temperature coefficients are of the same order of magnitude as those of the other substances in the table. Manganous chloride with 4 molecules of water of crystallization, and copper chloride with 2, form hydrates of the same degree of complexity as the other salts in this table. Their temperature coefficients are in keeping with this fact. The chloride of aluminium crystallizes with 6 molecules of water and the nitrate with 8. These salts, as has already been pointed out, break down yielding 4 ions each. Their temperature coefficients are larger than those of the ternary electrolytes.

The more dilute the solution, the more complex the hydrate formed by the molecule or the ion. This is but the expression of the action

[1]Carnegie Inst. Wash. Pub. No. 60, pp. 75, 76.

of mass; the more water there is present the more will be combined with the dissolved substance. The more complex the hydrate the greater the change in the complexity of the hydrate with rise in temperature. Since the magnitude of the temperature coefficients of conductivity seems to be a function of the change in the complexity of the hydrate with rise in temperature, it follows, from the hydrate theory, that the temperature coefficients of conductivity for any given substance should be greater at the higher dilution than at the lower.

A comparison of the results at the two dilutions for any given substance in table 48 or table 49 will show that the above consequence of the hydrate theory is confirmed by the facts. The temperature coefficients are larger at the higher dilution for every substance recorded in both tables.

One other relation should be pointed out before leaving the discussion of the temperature coefficients of conductivity. We have seen that the hydrates are unstable, and that with rise in temperature they break down. The higher the temperature to which they are heated the more unstable they become. We should, therefore, expect the hydrates to break down more rapidly as the temperature goes higher. If this were the case, the higher the temperature of the solution the larger the temperature coefficients of conductivity. If we compare the results for any given substance in table 48 or 49 we will find that such is the case. The temperature coefficients for any given dilution are higher between 50° and 65° than between 25° and 35°.

The above four conclusions from the solvate theory of solution, as far as aqueous solutions are concerned, are confirmed at every point by the results of measuring the temperature coefficients of conductivity. Without this theory it does not appear to be simple to explain the above relations. The agreement between the four deductions from the theory and the experimental results is so satisfactory that it is regarded as strong evidence in favor of the general correctness of the theory.

RELATION BETWEEN THE HYDRATION OF THE IONS AND THEIR IONIC VOLUMES.

Jones and Pearce[1] worked out the approximate composition of the hydrates formed by a large number of salts, using the freezing-point and conductivity methods already referred to. They found the following relation between the volumes of the ions and their power to form hydrates. The atomic volume curve is obtained by plotting the atomic weights of the elements as abscissæ against the atomic volumes as ordinates. This curve, as is well-known, contains well-defined maxima and minima. At the maxima are the alkali elements, the three with the largest atomic volumes being potassium, rubidium,

[1]Carnegie Inst. Wash. Pub. No. 180, p. 57; Amer. Chem. Journ., 38, 736 (1907).

and cæsium. The salts of these elements generally crystallize without water, and therefore have very little hydrating power in aqueous solution. The approximate hydration[1] of salts of potassium has been determined by the method usually employed and has been found to be small.

Some of the salts of lithium and potassium crystallize with 2 and 3 molecules of water, and these have been shown to have some hydrating power.[1] The atomic volumes of lithium and sodium are much smaller than those of potassium, rubidium, and cæsium.

Turning from the maxima of the curve to the minima, at the minimum of the third section of the curve are iron, cobalt, nickel, and copper. Salts of these metals crystallize with large amounts of water, and in aqueous solution they form complex hydrates.

Aluminium falls at the second minimum of the atomic volume curve, having a somewhat greater atomic volume than iron. The salts of aluminium crystallize with large amounts of water, some of them with 6 and 8 molecules. In aqueous solution they form complex hydrates.[1] Barium has the largest atomic volume of members of its group; its salts crystallize without water or some with 2 molecules of water. Many of the salts of calcium, strontium, and magnesium crystallize with 6 molecules of water. Magnesium has the smallest volume of any element of this group; it has been found to have the greatest hydrating power of any member of the group. Strontium has a slightly larger atomic volume than calcium and has a somewhat smaller power to form hydrates. Taking all of the facts into account, it would seem that, other things being equal, the smaller the cation the greater its hydrating power. This raises the question, which ion is it that forms the hydrate? Do both ions form hydrates. If so, which has the greater hydrating power?

The different salts of certain metals have approximately the same hydrating power. The common constituent of these salts is of course the cation, the anion varying from salt to salt. This would indicate that it is primarily the cation which conditions the hydrating power of a salt. Since the different salts of the same metal do not all have the same hydrating power, it seems reasonable to assume that the anion has some power to form hydrates in the presence of water. The cation is, then, the chief hydrating agent, and its hydrating power seems to be a function of its size or atomic volume—the smaller the ion the greater its power to hold water in combination with it in aqueous solution.

This raises the question, why is this the case? It has occurred to me that the electrical density of the charge on the ion may have something to do with this relation. Other things being equal, the smaller

[1]Carnegie Inst. Wash. Pub. No. 60.

ion has the greater density of charge upon its surface; this might enable it to hold more molecules of water in combination with itself. There seem, however, to be certain physical objections to this explanation of the relation in question. Whatever the explanation, the fact remains.

HYDRATION OF THE IONS AND THE VELOCITIES WITH WHICH THEY MOVE.

Certain apparent discrepancies presented themselves in the velocities of the different ions, which, for a time, could not be explained. It was known that the lithium ion, under the same driving force, moves more slowly than potassium; and yet it has smaller volume and smaller mass. It was not until it was shown[1] that the lithium ion is more strongly hydrated than sodium or potassium that this fact could be explained, and other apparent discrepancies presented themselves. A relation between the migration velocities of the ions and their hydrating power was worked out by Jones and Pearce.[2] Their discussion is repeated here to bring out the point in question.

The velocities of the ions in moving through any given medium is known to vary inversely as their mass, the driving force being constant. Their velocities would also vary inversely as their volumes. Mass being constant, we should expect the ions with the smallest atomic volumes to move the swiftest under a constant driving force, while the facts are often the opposite. Leaving out of account the hydrogen and hydroxyl ions, potassium, rubidium, and cæsium have very great velocities and the largest volumes; while the ions of the iron and copper group have the smallest volumes and very small velocities. The meaning of this apparent discrepancy can be seen at once by comparing the atomic volume curve and the migration velocity curve.

The ions with the smallest volumes have the greatest hydrating power. The ions with the smallest volumes frequently have the smallest velocities. Therefore, the ions with smallest velocities frequently have the greatest hydrating power. To discuss the relations somewhat in detail, the atomic volumes of potassium, rubidium, and cæsium increase rapidly with increasing atomic weight, and their salts generally crystallize without water. The atomic volumes of sodium and lithium are less than half that of potassium, and yet their velocities are only about two-thirds that of potassium. It will be recalled that salts of sodium and lithium may crystallize with 2 or 3 molecules of water. We may therefore assume that the increase in the volume and mass of the lithium and sodium ions, due to the formation of a hydrate, decreases the velocity of these ions below that of potassium.

The small velocity of the lithium ion was, as we have seen, for a long time unexplained. It has a volume only about half that of sodium, and the largest ascertained amount of water with which the salts of

[1]Carnegie Inst. Wash. Pub. No. 60. [2]*Ibid.*, 180, pp. 84–86.

lithium crystallize is 3. The maximum amount for many of the salts of sodium is 2. The lithium ion is, in general, more hydrated than the sodium ion, and its velocity is therefore decreased more by hydration. Notwithstanding its smaller volume and lighter mass, on account of its greater hydration lithium moves with about the same velocity as sodium.

The calcium ion is slightly larger than sodium, but has considerably smaller velocity. This is undoubtedly due primarily to its much greater hydrating power. Within this group the atomic volumes increase with increasing atomic weight. The velocities of calcium and strontium, with many salts crystallizing with 6 molecules of water, are approximately equal to that of barium. Many of the salts of barium crystallize with 2 molecules of water or water-free. The larger mass of the barium ion itself diminishes the velocity. Magnesium, with about half the volume of calcium, has nearly the same velocity, due to its greater hydrating power. The cobalt, nickel, and copper ions have nearly the same volumes and approximately the same hydrating power. They have approximately the same velocities.

The atomic volumes of the chloride, bromide, and iodide ions are approximately the same. If they hydrate at all we should expect the same order of hydration for all three, as has been made probable. We should expect them to have velocities of the same order of magnitude, and such is the fact.

The silver ion is the only well-established exception. It has a small volume and many of its salts crystallize without water. Although it has small volume, it apparently has but little hydrating power. Notwithstanding its considerable mass, with its small volume and small hydrating power we should expect it to have a fairly high velocity. The fact is, the velocity of the silver ion is slightly less than that of chlorine, bromine, and iodine.

The general truth of the relation that the ions with the smallest velocities have the greatest hydrating power is, then, established by the facts, the great hydrating power being one of the factors conditioning the small velocity.

DISSOCIATION AS MEASURED BY THE FREEZING-POINT METHOD AND BY THE CONDUCTIVITY METHOD.

When the theory of electrolytic dissociation was proposed, it became a problem to measure accurately the magnitude of dissociation. Arrhenius pointed out, in his original epoch-making paper, that dissociation could be measured either by the freezing-point or by the conductivity method. The conductivity of a few electrolytes was first worked out accurately by Friederich Kohlrausch, by a method which he devised for the purpose. This work was done before the theory of electrolytic dissociation was proposed. Kohlrausch's data were

used to calculate the magnitude of the dissociation of the electrolytes with which he worked, at the various dilutions of the solutions.

Another method of measuring the dissociation of electrolytes, based upon the change in the solubility of a salt on the addition of a second salt with a common ion, was developed theoretically by Nernst[1] while working in Ostwald's laboratory. When applied experimentally it gave dissociations which were different from those obtained by the conductivity method. The freezing-point method had not been used at that time to measure dissociation. There was then a period when there were but two methods for measuring dissociation, and these gave widely different results. During this period the point was made against the dissociation theory, that if dissociation took place in the presence of water there was no means of determining its magnitude.

At this time Ostwald so improved the freezing-point method that it could be used to measure dissociation. He started me to work on the application of this method, and we[2] measured the dissociation of a fairly large number of salts. The results differed radically from those obtained by the solubility method, but agreed fairly well with those calculated from the conductivity method of Kohlrausch. It was afterwards shown that an assumption had been made in applying the solubility method, which, when corrected, enabled that method to give essentially the same results as those obtained by the other two.

A comparison of the data from the freezing-point method with those from the conductivity method showed that dissociation as measured by the former was slightly higher than by the latter. The meaning of this discrepancy was at that time not understood.

After it had been established, with reasonable certainty, that hydration takes place in aqueous solution, a possible explanation of this apparent discrepancy presented itself. But before offering this explanation it seemed desirable to do more experimental work, having this point especially in mind. Pearce[3] carried out in my laboratory a very careful piece of work, in which dissociation was measured by the freezing-point method and also by the conductivity method, and the two sets of results were compared. We worked with the chlorides of calcium, strontium, magnesium, barium, cobalt, copper, and aluminium; with the nitrates of calcium, magnesium, barium, cobalt, nickel, and copper; with sodium bromide, and with hydrochloric, nitric, and sulphuric acids.

That hydration can explain the fact that dissociation as measured by freezing-points is higher than as measured by conductivity can be seen from the following. The combined water is removed from the field of action as solvent; only the uncombined water is acting as solvent. Freezing-point lowering is proportional to the ratio between

[1]Zeit. phys. Chem., **4**, 1372 (1889).
[2]*Ibid.*,**11**, 110, 529; **12**, 633 (1893).
[3]Carnegie Inst. Wash. Pub. No. 180, p. 57.

the number of molecules of the dissolved substance and of the solvent. If one-fourth of the water present is combined with the dissolved substance, the freezing-point lowering would be one-fourth greater than if all the water were present as free water and therefore acting as solvent water. Freezing-point lowering would thus be affected proportionally by hydration. Dissociation of concentrated solutions calculated from the freezing-point lowering would therefore be much too high.

The conductivity of a solution depends upon the number of ions present and their velocities. The number of ions would probably not be affected greatly by the hydration, but their velocities would be. The hydrated ions, would, of course, move more slowly than the unhydrated.

The effect of hydration would obviously be more pronounced on freezing-point lowering, which is proportional to the amount of solvent present, than on conductivity. The following results taken from the work of Pearce[1] will show that this conclusion is justified:

TABLE 50.—*Dissociation from freezing-point lowering and from conductivity.*

Salt.	Concentration.	Dissociation from freezing-point lowering.	Dissociation from conductivity.	Salt.	Concentration.	Dissociation from freezing-point lowering.	Dissociation from conductivity.
$CaCl_2$.....	0.01	.....	89.67	$CoCl_2$.....	0.05	90.28	84.80
	0.05	85.00	80.62		0.10	87.36	78.85
	0.10	80.41	74.35	$Mg(NO_3)_2$.....	0.02	94.90	85.12
$SrCl_2$.....	0.01	91.87	89.37		0.05	84.24	78.80
	0.05	82.65	78.10		0.10	81.95	74.78
	0.10	81.46	74.17	$Ba(NO_3)_2$.....	0.01	99.06	86.37
$BaCl_2$.....	0.01	97.10	90.90		0.05	75.18	70.47
	0.05	90.75	79.80		0.10	62.95	61.36
$MgCl_2$.....	0.01	97.10	90.90	$Co(NO_3)_2$	0.01	98.65	92.40
	0.05	90.75	79.78		0.05	88.26	81.73
	0.10	87.68	73.61		0.10	85.48	76.48
$SrCl_2$	0.01	91.87	89.37	$Ni(NO_3)_2$.....	0.01	98.03	91.10
	0.05	82.65	78.08		0.05	83.72	79.83
	0.10	81.46	74.17		0.075	81.32	76.57

Concentrated solutions were also studied in the above work; but on account of very large hydration it was impossible to calculate dissociation from the freezing-point results.

An examination of the above table will show that the dissociation of dilute solutions, as measured by the freezing-point method, is uniformly greater than as measured by the conductivity method. This seems to admit of reasonable explanation in terms of hydration in aqueous solution.

[1]Carnegie Inst. Wash., Pub. 180; Amer. Chem. Journ., **39**, 313 (1908).

EFFECT OF ONE SALT WITH HYDRATING POWER ON THE HYDRATES FORMED BY A SECOND SALT IN THE SAME SOLUTION.

The effect of adding a salt with strong hydrating power to a solution of another strongly hydrated salt was worked out by Jones and Stine.[1] The effect of adding a salt with small hydrating power was also investigated. The following pairs of salts were studied: Calcium chloride and potassium chloride; magnesium chloride and calcium chloride; strontium chloride and calcium chloride; strontium nitrate and magnesium nitrate; calcium nitrate and magnesium nitrate; aluminium chloride and ferric chloride; calcium chloride and calcium nitrate; lithium bromide and sodium bromide, and ammonium chloride and potassium chloride, as examples of only slightly hydrated salts.

A large variety of types of salts was used. The first pair contains a binary and a ternary electrolyte with a common anion; the one (calcium chloride) strongly hydrated, the other (potassium chloride) only slightly hydrated. The next four pairs are all ternary electrolytes and are all strongly hydrated salts.

Aluminium chloride and ferric chloride are quaternary electrolytes and strongly hydrated. The two calcium salts contain a common cation and both are strongly hydrated. The two bromides contain a common anion and are not strongly hydrated, while the chlorides of ammonium and potassium are very weakly hydrated compounds.

The problem was obviously a complicated one. It was not a simple matter to calculate the composition of the hydrates formed by any one substance when present alone in the solution. It became far more complex and difficult to calculate the composition of the hydrates formed when two hydrating substances were present simultaneously in the solution. We believe, however, that this problem was solved at least approximately. It was found that the amount of combined water increases with increase in concentration in the mixed, as in the separate solutions; the total amount combined with the calcium chloride being less when the potassium chloride was present. The difference between the amount of water combined with the calcium chloride when alone and when potassium chloride is present increases with the concentrations of the two constituents of the mixture.

We found in general that when two hydrated salts were mixed, each dehydrated the other to an amount that seemed to be controlled by mass action. In order that this law should hold, it would seem that the calculated composition of the hydrates formed by the individual substances must be approximately correct.

It was early found that both ions and molecules can form hydrates. That the molecules of certain substances have hydrating power, was shown by the fact that certain non-electrolytes undoubtedly combine with water in aqueous solution. Ions were, as a class, found to have

[2]Amer. Chem. Journ., **39**, 313 (1908).

much greater hydrating power than molecules. This conclusion was confirmed by the work of Stine. It was also shown that molecules in aqueous solution can combine with water, and in special cases molecules may even have greater hydrating power than some ions.

The work with the slightly hydrated potassium and ammonium chlorides brought out a significant fact. These were chosen, not to study the effect of one hydrated salt on the hydration of another hydrated salt, but to study the effect of change in temperature on the conductivities of separate solutions of electrolytes and upon mixtures of these solutions. For this purpose it was necessary to select a pair of salts with small hydrating power and also which do not form double salts with one another.

If suppression of ionization were the only cause of the diminution in conductivity on mixing solutions of salts, such as the above, which have a common ion, then we should find the greatest dimunition where the dissociation is greatest. Since dissociation is slightly greater at 0° than at 12°, and slightly greater at 12° than at 25°, we should expect to find greater diminution in the conductivity at 0° than at 12°, and greater at 12° than at 25°. Exactly the reverse is true.

Again, as the difference in dissociation between 0° to 12° is but little greater than between 12° and 25°, we should expect to find that between these two ranges of temperature the driving back of the conductivity would be of the same order of magnitude, yet such is not the case.

Furthermore, some of the solutions which we mixed are nearly isohydric, and such solutions do not drive back each other's dissociation. Driving back the dissociation of a salt by the addition of a second salt with a common ion is, therefore, not the only cause of the diminution in conductivity which results when salts with a common ion are mixed.

It was pointed out that three other factors may come into play: (1) Change in hydration giving rise to change in the size and mass of the ion, which probably plays a very insignificant role in the above-named case, since the chlorides of ammonium and potassium are only slightly hydrated. (2) Change in the number of the dissolved parts, which, however, is not very large for small changes in temperature. (3) Change in the viscosity of the solution with change in temperature, which is undoubtedly a very prominent factor, hitherto either overlooked or not given sufficient prominence in dealing with the phenomenon in question.

INVESTIGATIONS IN MIXED SOLVENTS.

The study of the conductivities and dissociations in pure solvents was extended here to mixed solvents. This phase of the work has now been in progress continuously for a dozen years, and the results have been published in monographs Nos. 80 and 180 of the Carnegie Institution of Washington.

The first investigation was carried out by Lindsay.[1] He worked in water, in methyl, ethyl, and propyl alcohols, and in mixtures of these solvents with one another. He found, in certain mixtures of the alcohols with water, that the conductivity of the dissolved salt was less than in the pure alcohol. The conductivity curves in mixtures of methyl alcohol and water passed through well-defined minima, and a conductivity minimum was also frequently found in mixtures of ethyl alcohol and water.

A possible explanation of the results in mixtures of the alcohols with water is that each solvent diminishes the association of the other. Since the dissociating power of a solvent is in general greater the larger its own association, it follows that whatever would decrease the association of a liquid would decrease its power to dissociate electrolytes dissolved in it. The question is, does one associated liquid diminish the association of another associated liquid?

An associated liquid tears down the molecules of an electrolyte dissolved in it, into simpler parts or ions; and it might be expected that such a liquid would tear down the molecules of another associated liquid, a non-electrolyte, not into charged parts or ions, but into simpler molecules. The alcohol and water are associated liquids, as has been shown by the surface-tension method of Ramsay and Shields.[2] Do these diminish the association of one another?

That this is the case was shown by Murray.[3] He worked with the associated liquids, water, formic acid, and acetic acid. He determined the molecular weight of each of these liquids in the other two, and found that their molecular weights became smaller the more dilute the solutions. This showed that the solvent, *i. e.*, the liquid present in the larger quantity, was tearing down the molecular complexes of the dissolved liquid or the one present in smaller quantity.

That the diminution in the association of one associated liquid by another associated liquid was true, was shown for the above-named substances and made highly probable for others.

That this was not the entire explanation of the nature of the conductivity curves in mixtures of certain alcohols with water, was brought out by the next investigation in this field, carried out here by Carroll.[4] He compared the conductivity curves of electrolytes dissolved in these solvents, with the fluidity curves of the mixtures of the two liquids in question, and found that the two sets of curves were very similar. The minima in the two cases occurred in the same mixture of the two liquids. A careful comparison of the two sets of phenomena led us to conclude that the conductivity minima are largely due to the diminished fluidity which takes place on mixing the two solvents. The diminished fluidity, or increased viscosity, would cause the ions to move more slowly, and hence decrease the conductivity.

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[1] Amer. Chem. Journ., **28**, 329 (1902).
[2] Zeit. phys. Chem., **12**, 433 (1893).
[3] Amer. Chem. Journ., **30**, 193 (1903).
[4] *Ibid.*, **32**, 521 (1904).

At the end of the work done by Carroll, we seemed justified in concluding that the conductivities of binary electrolytes in such solvents as those already considered, are inversely proportional to the coefficients of viscosity of the solvent and are directly proportional to the association of the solvent. Bassett[1] showed that silver nitrate in mixtures of methyl alcohol and water gave a conductivity minimum at both 0° and 25°; also that the effect of one solvent on the other was greater at 0° than at 25°. This would be expected, since the dissociation diminishes with rise in temperature, and each solvent would probably diminish the association of the other less, the smaller its own association or the higher its temperature.

Bingham[2] not only measured the conductivities, but also the viscosities of a number of solvents and solutions in these solvents. He found minima in the conductivity curves in mixtures of acetone and water. The distinctly new feature brought out by the work of Bingham was that lithium and calcium nitrates in mixtures of acetone with methyl and ethyl alcohols showed a pronounced maximum in the conductivity curves. This must be due either to an increase in dissociation in such mixtures, increasing the number of ions present, and consequently increasing the conductivity, or it must be due to a diminution in the complexity of the solvates around the ions, increasing their velocities. The dissociation was measured in the mixtures in question and found not to account for the phenomenon. This eliminates increase in dissociation and leaves the other alternative, diminution in the complexity of the solvate, to account for the phenomenon.

The ion must drag with it through the solvent any molecules of the liquid with which it had combined. This would increase the effective mass and diminish its velocity. Anything which would diminish the complexity of the solvate about the ion would increase its velocity, and consequently the conductivity. We must therefore conclude that the solvates in those mixtures of acetone with the alcohols are simplest where the conductivity is the greatest.

Rouiller[3] studied both the velocities of the ions and the conductivities of electrolytes in mixtures of acetone with the alcohols. Silver nitrate in methyl alcohol and acetone gave a decided maximum of conductivity. His work on the velocities of the ions in these mixtures indicated that the above explanation of the maxima offered by Jones and Bingham was correct; there is a change in the complexity of the solvate about the ion.

McMaster[4] extended the work in the same solvents used by Bingham—water, methyl alcohol, ethyl alcohol, and acetone—and in mixtures of these with one another. He found conductivity results of the same general character as those obtained by the earlier workers. Conduc-

[1] Amer. Chem. Journ., **32**, 409 (1904).
[2] *Ibid.*, **34**, 481 (1905).
[3] *Ibid.*, **36**, 443 (1906).
[4] *Ibid.*, 326 (1906).

tivity minima were found in mixtures of the alcohols with water and acetone with water. Conductivity maxima were obtained with lithium bromide in mixtures of methyl or ethyl alcohol with acetone. Cobalt chloride in mixtures of acetone with ethyl alcohol also showed a maximum. Jones and McMaster reached the same conclusion from their work that had been reached by Jones and Bingham. Change in the complexity of the solvate formed by the ion in different mixtures of solvents is an important factor in determining the conductivity maxima.

A point of interest brought out by the work of McMaster was in connection with the temperature coefficients of conductivity in non-aqueous solutions. The bearing of temperature coefficients of conductivity on the solvate theory of solution has already been discussed. With rise in temperature the hydrates about the ions became simpler. The mass and probably the size of the ion thus became less, and it moves faster the higher the temperature, thus increasing the conductivity.

McMaster found that cobalt chloride in certain mixtures of acetone with the alcohols showed, at ordinary temperatures, negative temperature coefficients of conductivity. What does this mean? The solvent becomes less viscous with rise in temperature, thus increasing the velocity of the ions; and the solvates become simpler, which also increases the velocity with which the ions move.

With rise in temperature, on the other hand, the association of the solvent, and consequently its dissociating power, becomes less.

The above two influences work counter to one another. Negative temperature coefficients of conductivity mean that the latter influence overcomes the former. The alcohols used and acetone are highly associated liquids. Rise in temperature diminishes their association and consequently their dissociating power.

A solution of cobalt chloride in a 75 per cent mixture of acetone with methyl alcohol, the solution being $\frac{1}{200}$ normal, had a zero temperature coefficient of conductivity.

A number of points of interest were brought out by the next investigator, Veazey.[1] He worked with solutions of salts in water, methyl alcohol, ethyl alcohol, acetone, and in binary mixtures of these solvents with one another. The minimum in conductivity was found to be a more general phenomenon than had been supposed from the earlier work. It had long been known that mixtures of methyl alcohol and water or ethyl alcohol and water, are more viscous than either of the pure solvents alone. A rational explanation of this phenomenon was suggested—alcohol and water are strongly associated liquids. When two associated liquids are mixed each diminishes the association of the other. The larger molecules are thus broken down into smaller molecules, which increases the frictional surfaces when these molecules move over one another as they do in measuring viscosity. The result

[1]Amer. Chem. Journ., **37**, 405 (1907). Zeit. phys. Chem., **61**, 641 (1908); **62**, 44 (1908).

would be to increase the viscosity of the mixture over that of either pure solvent.

Maxima in the conductivity of electrolytes in the mixed solvents were shown to correspond to maxima in the fluidity of the mixed solvents. Maxima in fluidity are probably due to an increase in the size of the molecules of the solvent, due to a combination of one solvent with the other. This would diminish the viscosity and consequently increase the velocity of the ions, which would increase the conductivity. This factor must also be taken into account in explaining conductivity maxima.

The temperature coefficients of conductivity in the above-named mixtures of liquids with water are a maximum in the 25 and 50 per cent mixtures. These are just about the mixtures in which the solvents have the least association. The molecules of the solvents being in the simplest condition, would be most favorable for chemical action. In such mixtures the solvents probably combine to the greatest extent with the dissolved substance—the solvation is at a maximum. The effect of rise in temperature breaking down these solvates would therefore be a maximum where solvation is a maximum. Solutions of potassium sulphocyanate have greater conductivity in acetone than in water. This was shown to be due to the greater fluidity of the acetone.

This same salt when dissolved in water lowers the viscosity of the water. An examination of the literature showed that certain salts of potassium and salts of rubidium and cæsium are practically the only ones known to lower the viscosity of water. In the case of certain salts of potassium the positive effect of the anion on the viscosity of water may more than offset the negative effect of the potassium ion.

The following explanation of the above-named phenomenon was suggested. If the atomic volume of the ions dissolved in the solvent was larger than the molecular volume of the solvent, the larger ions would diminish the size of the frictional surfaces coming in contact and would lower the viscosity.

It is well known that potassium, rubidium, and cæsium occupy the maxima on the atomic-volume curve, and have much larger atomic volumes than any other known elements. Potassium has a smaller atomic volume than rubidium, and rubidium than cæsium. Potassium chloride lowers the viscosity of water less than rubidium chloride, and rubidium chloride less than cæsium chloride.

If we study the salts which raise the viscosity of water, we will find, in general, that the amount of increase in the viscosity bears a relation to the atomic or ionic volumes of the dissolved substances. Smaller ions tend to increase the viscosity of water more than larger ones. It would therefore seem that the above explanation contains a large element of truth.

The work already discussed in mixed solvents is all recorded in Publication No. 80 of the Carnegie Institution of Washington. The results of the following five investigations are recorded in Publication No. 180 of the Carnegie Institution of Washington.

The problem of measuring dissociation in non-aqueous solvents is a difficult one. The freezing-point method is frequently not applicable. Many common solvents, such as the alcohols, freeze at temperatures which are too widely removed from the ordinary temperature of the laboratory to measure with sufficient accuracy. The boiling-point method could be used only with fairly concentrated solutions. Dilute solutions produce such a slight rise in the boiling-point that this small quantity can not be measured with a very high degree of accuracy. The boiling-point method has the further disadvantage of being so largely affected by slight changes in the barometer.

The hope of measuring conductivity in non-aqueous solvents in general seemed to rest in the conductivity method. This method as ordinarily applied would not be satisfactory. The dilution at which complete dissociation would be reached in such solvents is so great that the Kohlrausch method in any such form as he left it could not be applied to the problem.

The conductivity method was greatly improved by Kreider;[1] the greatest improvement being in the form of cell employed. With the improved method Kreider studied the dissociations of a number of salts in methyl and ethyl alcohols and in mixtures of these solvents with water. He measured the conductivities of solutions as dilute as 100,000 liters.

He found the following relation: $\frac{\mu_\infty \text{ methyl alcohol}}{\mu \text{ ethyl alcohol}} = \text{constant.}$

When a salt is dissociated in each of two solvents, for the same concentration of the salt there are the same number of ions in the two solutions. Conductivity is a function of the number of the ions and their velocities. When numbers of the ions are constant, as in this case, conductivity is a function of the relative velocities of the ions. The velocity of an ion is conditioned by its mass and volume and by the fluidity of the solvent. If the masses and volumes of the ions in the two solvents are constant, the velocities of the ions should vary as the fluidities of the solvents. The ratio between the values of μ_∞ in the two solvents should be the same as the ratio between the fluidities of these solvents. This was, however, found not to be the case. The bearing of this fact on the condition of the ions in the two solvents in question is important. This shows that the mass and probably the volume of the solvated ion must differ in the two solvents.

The ratio between the values of μ_∞ for a salt in the two solvents, compared with the ratio between the fluidities of the two solvents,

[1]Amer. Chem. Journ., **45**, 282 (1911).

would give an approximate idea of the relative solvation of the ions in the two solvents in question.

This method will be still further applied to the problem of solvation in non-aqueous solvents.

Mahin[1] studied electrolytes in ternary mixtures of the alcohol with water, and obtained results of the same general character as those found in binary mixtures of these solvents. He then took up work in binary mixtures, one constituent being acetone. Acetone was studied primarily because it is an exceptional solvent in many of its properties. Substances dissolved in acetone are largely polymerized, and acetone has at the same time considerable dissociating power. Furthermore, acetone is a solvent with small viscosity, and it was desired to see whether the relations found for solvents with larger viscosity would hold here. The curve for conductivity and for fluidity were worked out and the two compared.

It was found that the product of molecular conductivity and viscosity is nearly a constant at complete dissociation. This means that for completely dissociated solutions in acetone the curves of molecular conductivity are similar to those of fluidity—conductivity being inversely proportional to viscosity. This relation is of interest in that it holds in a solvent with such small viscosity as acetone.

Relations such as those referred to above having been found to hold in a solvent with such small viscosity as acetone, the question arose, do such relations obtain in a highly viscous solvent like glycerol? Glycerol not only has a very high viscosity, but is an excellent solvent, and has a large dielectric constant, which means that it has considerable dissociating power. Glycerol is fairly strongly associated, which also indicates considerable dissociating power.

The first investigation in glycerol as a solvent was carried out by Schmidt.[2] He measured the conductivities of solutions of certain salts in glycerol, and in mixtures of glycerol with water and with methyl and ethyl alcohols. The conductivities were measured at different temperatures. The most striking relation noted was the enormous magnitude of the temperature coefficients of conductivity of electrolytes dissolved in glycerol. This was shown to be due to the rapid decrease in the viscosity of glycerol with rise in temperature.

It was shown that where glycerol is mixed with water or the alcohols, there is a breaking down of the association of each solvent by the other, and a consequent diminution in the dissociating power. Solutions of potassium iodide in 25 and 50 per cent mixtures of glycerol and water lowered the viscosity of these solvents. This salt does not lower the viscosity of glycerol, but of the mixtures. The meaning of negative viscosity effects was discussed in the work of Veazey. While Schmidt did not study any salt which lowers the viscosity of pure glycerol, he

[1]Amer. Chem. Journ., **41**, 433 (1909); Zeit. phys. Chem., **69**, 389 (1909).
[2]Amer. Chem. Journ., **42**, 37 (1909).

found that the effect of the salt on the viscosity of pure glycerol was inversely as the molecular volume or atomic volumes of the constituents of the salt. This was in keeping with the explanation offered by Jones and Veazey to account for the changes in the viscosity of the solvent by the dissolved substance. A comparison of the conductivity and fluidity curves shows that the two run nearly parallel. Although glycerol has about 1,000 times the viscosity of methyl alcohol, yet, from the work of Schmidt, the same general relations obtain here that hold for the far less viscous solvents.

The work of Schmidt was continued by Guy.[1] He worked with a much larger number of salts, and over the temperature range 25° to 75°. He studied not only solutions in glycerol, but in mixtures of glycerol with water, with methyl, and with ethyl alcohols.

Guy found also enormous temperature coefficients of conductivity. This may be due to either of two causes: a change in dissociation with rise in temperature, or a change in the velocity of the ions. We know the order of magnitude of the change in dissociation with rise in temperature, and it is small. The chief cause of the large temperature coefficients of conductivity in glycerol is, then, an increase in the velocities with which the ions move. As we have seen, this may be due to a decrease in the viscosity of the solvent with rise in temperature, or may be caused by a breaking down of complex solvates about the ions.

While the viscosity of glycerol increases rapidly with rise in temperature, this alone would not account for the magnitude of the temperature coefficients of conductivity of glycerol solutions. There seems to be good evidence for the formation of glycerolates in solutions in glycerol. The temperature coefficients of conductivity in glycerol are greater at high than at low dilution. Jones has pointed out that this would be expected from the solvate theory. The more dilute the solution the more complex the solvate; the more complex the solvate the greater the change in its complexity with rise in temperature.

Further, salts of calcium, strontium, and barium have larger temperature coefficients of conductivity than those of sodium, potassium, and ammonium. The former are strongly hydrated, the latter weakly hydrated substances. It would seem that the former are more strongly glycerolated than the latter. Salts which have approximately the same hydrating power have temperature coefficients of conductivity in glycerol of the same order of magnitude, indicating the same order of magnitude of glycerolation. Work in the mixed solvents indicates that water diminishes the association of glycerol.

Solutions of salts in glycerol have in general greater viscosity than pure glycerol. Guy, however, found marked exceptions to this relation. Salts of rubidium lowered the viscosity of glycerol. Ammonium bromide and iodide also lowered the viscosity of this solvent. That

[1]Amer. Chem. Journ., 46, 131 (1911).

rubidium should lower the viscosity of glycerol is in keeping with what was found in aqueous solutions. Salts of rubidium and cæsium and some salts of potassium lowered the viscosity of water. This has already been explained as due to the large atomic volumes of these elements. The same explanation holds for solutions in glycerol.

Davis[1] continued the work of Guy, studying especially the effect of salts on the viscosity of glycerol. He repeated the work with ammonium iodide and obtained the same result that had been earlier found by Guy. He studied rubidium chloride, bromide, iodide, and nitrate, and showed that these lowered the viscosity of glycerol. The rubidium salts lower the viscosity of glycerol to such an extent that they appreciably increase their own conductivity in this solvent.

Comparing the effects of the chloride, bromide, and iodide of rubidium on the viscosity of glycerol, Davis found that the chloride has the least effect, the bromide next, the iodide the greatest. He showed that this was in the same order as the molecular volumes of the salts in question. The results obtained with glycerol were, then, analogous to those obtained with water, both with respect to viscosity and solution.

SPECTROSCOPIC EVIDENCE BEARING ON THE SOLVATE THEORY OF SOLUTION.

WORK OF JONES AND UHLER.

Work on the absorption spectra of solutions has now been in progress in my laboratory continuously for eight years. This work was undertaken in connection with its bearing on the solvate theory of solution. What connection is there between solvation and the power of solutions to absorb light?

It is well known that absorption of light means that the wave-lengths of light set something vibrating with periods the same as their own. Selective absorption of light or the absorption of certain wave-lengths of light means that the wave-lengths absorbed set something vibrating with their own periods. Absorption of light is, then, a resonance phenomenon. Absorption of light by a dissolved substance means that something in the solution must be thrown into resonance with the light—must be set vibrating with the same periods as the light-waves. Many dissolved substances absorb only certain wave-lengths. This means that those particular wave-lengths of light find something in the solution which they can set vibrating with their own periods. Transparency means lack of resonance, opacity means resonance. The color of any given solution is determined by the wave-lengths of light which are not absorbed. A red solution is one which allows the long wave-lengths to pass through. A blue solution is one which allows the short wave-lengths to pass through. That particle in solution which is thrown into resonance by the light is called the

[1]Zeit. phys. Chem., **81**, 68 (1912).

resonator. This was formerly supposed to be the molecule or the ion, but is now thought to be the electron. Whatever the nature of the resonator, the absorption of light by dissolved substance is due to it.

The line of thought which led us to take up the study of the absorption spectra of solutions in connection with the solvate theory of solution is the following: The absorption of light being due to a resonator, this would have different resonance when anhydrous than when combined with molecules of the solvent. In general, the resonance would be different when the resonator was unsolvated than when it was solvated. The color of the solution being due to the resonator, the solution could reasonably be expected to have different color when the resonator was solvated than when it was unsolvated. The study of the color of solutions, and the changes in the color when the resonator underwent changes in solvation, might give some clue to the changes in solvation.

It is a comparatively simple matter to change solvation in solution; it is only necessary to change the concentration of the solution. The more dilute the solution the more complex the solvates formed. We shall see that this often produces a marked change in the absorption spectra. We can diminish the complexity of the solvates by raising the temperature. This also frequently produces marked changes in the absorption. Addition of a dehydrating agent will change the hydration of any given salt. This frequently changes the absorption spectra and the color of a solution; and there are many other ways of changing solvation. These frequently produce concomitant changes in the absorption spectra.

A salt dissolved in water may form hydrates, in alcohol alcoholates, in acetone acetonates, in glycerol glycerolates, etc. We should expect these different solvates to affect the resonator or resonators differently. We shall see that this is true.

With this idea in mind, work was begun in my laboratory on the study of the absorption spectra of solutions. The first investigation was carried out by Dr. Uhler and myself. Our work consisted largely in devising a method and apparatus for studying the property of solutions to absorb light. The key to the method consisted in using a grating instead of a prism spectroscope. This gave much greater dispersion, and brought out many new lines and bands. A form of cell was devised for holding solutions in non-aqueous solvents which avoided the use of all cement. The details of this phase of the work are all given in Publication No. 60 of the Carnegie Institution of Washington. We studied the effect on the absorption spectra of increasing the concentration of the solution, and found that, in general, the effect of increasing the concentration of the solution was to widen the absorption bands. As the solvates became simpler the absorption bands became broader.

Another method of simplifying the hydrates existing in an aqueous solution was to add a dehydrating agent in the form of a second salt.

It was found that this also produced a widening of the absorption bands. This was in keeping with the effect of increasing the concentration of the solution, which also simplified the hydrates.

Jones and Uhler also studied the effect of adding water to solutions in non-aqueous solvents. Thus, water was added to solutions in methyl and ethyl alcohols, acetone, etc. The effect of adding water was to narrow the absorption bands. All of these results were regarded as in keeping with the solvate theory of solution.

WORK OF JONES AND ANDERSON.

The work of Jones and Uhler on the absorption spectra of solutions was greatly extended in a number of directions by Jones and Anderson.[1] They worked with salts of cobalt, nickel, copper, iron, chromium, neodymium, praseodymium, and erbium. Only that phase of the work will be discussed here which bears on the solvate theory of solution.

We will first consider the results with salts of cobalt. There is a region of one-sided absorption in the ultra-violet. This band narrows with dilution, but remains of approximately constant width when the number of molecules in the path of the beam of light is kept constant, indicating that the absorbers here are the undissociated molecules.

The band λ3300 disappears rapidly with increase in the dilution of the solution, even when the number of molecules in the path of the beam of light is kept constant. This band increases rapidly in intensity with rise in temperature, and can be accounted for best by assuming that it is due to a relatively simple hydrate. It is well known that rise in temperature breaks down complex hydrates into simpler ones, which would give rise to the band; and, further, increase in dilution produces more and more complex hydrates. These would cause the disappearance of a band due to simpler hydrates.

The green cobalt band can not be due to the cobalt ions, since it is not most intense where the number of cobalt ions is the greatest. The width of this band does not vary, if the light is passed through such depths of the solution that the product of the concentration multiplied by the depth is kept constant. This would indicate that this band is due to the cobalt atom, whether combined as in the molecule or dissociated as an ion.

The absorption in the red is characteristic of concentrated solutions alone. This would show that it is not due to the cobalt ion. We might suppose that it was due to aggregates of molecules; but this view is not tenable, since the absorption in the red increases with rise in temperature, which breaks down such aggregates. High temperature and great concentration favor the formation of simple hydrates and also increase the absorption in the red. The red absorption can therefore be accounted for as due to simple hydrates in solution.

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[1]Carnegie Inst. Wash. Pub. No. 110; Amer. Chem. Journ., **41**, 163 (1909).

Jones and Anderson also did some work on the absorption spectra of cobalt salts in certain non-aqueous solvents. The green band appeared in all of the non-aqueous solutions studied. This is just what would be expected if this band is due to the cobalt atom. The intensity of this band in non-aqueous solvents was found to be proportional to the concentration.

The red absorption is more intense in the non-aqueous solvents than in water, the intensity increasing from methyl alcohol to ethyl alcohol to acetone. With increase in the dilution the band narrows rapidly in methyl alcohol, more slowly in ethyl alcohol, and remains nearly constant in acetone. All of these facts are in accord with the view that this band is due to simple solvates. We should expect the power to form solvates to be greater for methyl alcohol than for ethyl alcohol, and greater for ethyl alcohol than for acetone. In ethyl alcohol and acetone at ordinary temperatures most of the solvates are probably simple enough to absorb in the red, while in methyl alcohol this is the case only at elevated temperatures or in concentrated solutions.

The nickel absorption bands are similar in their behavior to the green band of cobalt. The absorption of nickel salts seems to be largely a function of the nickel atom. The widening of the band λ 3960, with concentration and with hydrating agents, indicates that the simplest hydrates have a somewhat different absorption from the more complex. The ultra-violet absorption of copper salts decreases rapidly with dilution, when we keep the product of depth of layer and concentration constant. This would indicate that this absorption is not due to the ions, but must be due in some way to the molecules. The absorption decreases with the dilution, even when the molecules in the path of the light are kept constant. This would indicate that the absorbing power of molecules is affected by the surroundings.

The increase in the absorption with concentration when the molecules are kept constant might be due to the formation of molecular aggregates or might be due to solvates. To decide between these two alternatives we must take into account the effect of rise in temperature on the absorption. Rise in temperature increases the absorption, but rise in temperature breaks down the molecular aggregates. Therefore, this absorption can not be due to aggregates. Solvates become simpler both by rise in temperature and by increase in the concentration of the solution. Both should produce the same effect on the absorption if this absorption is due to simple solvates, and such is the fact. We must therefore conclude that the ultra-violet absorption of copper salts is due to simpler hydrates.

For equal concentration the ultra-violet absorption of copper salts is least in the aqueous solutions, and increases as we pass from methyl to ethyl alcohol. Further, the change in this absorption with dilution is greatest for the aqueous solutions, and decreases as we pass to methyl

and ethyl alcohols. These facts are just what would be expected if this absorption was due to simpler solvates, since the power to form solvates is greater for water than for either of the alcohols, and greater for methyl than for ethyl alcohol. For equal concentrations the solvates would decrease in complexity as we pass from water to methyl alcohol. Further, increase in dilution would change the complexity of the solvates more in aqueous solutions than in solutions in either of the alcohols. The above conclusion is, then, in perfect accord with all of the facts.

The absorption of copper salts in the red narrows when the product of concentration and depth of absorbing layer is kept constant, but widens when the molecules are kept constant. Its intensity varies far more with change in concentration than with change in solvent. This absorption must be due to the atom, and is affected comparatively slightly by the surroundings of the atom. The copper absorption in the red is, then, less affected by solvates than the absorption by copper in the ultra-violet. The feature of the work of Jones and Anderson, which bears most directly on the solvate theory of solution, came out as the result of studying the absorption spectra of solutions of salts of neodymium and praseodymium, and especially of neodymium.

Neodymium chloride was found to have quite different absorption in water from what it had in methyl alcohol. This made it desirable to study the absorption spectrum of this salt in mixtures of methyl alcohol and water. By changing the composition of the mixtures of the two solvents, we could see how the spectra corresponding to the two solvents would change.

It was found that when the proper mixture of alcohol and water was used, the two spectra (the one corresponding to the alcoholic solution and the other to the aqueous solution) coexisted on the plate. When the amount of water in the mixed solvents increased, the "water spectrum" came out more strongly; when the amount of alcohol present was increased, the "alcohol spectrum" came out more strongly. When the amount of water present exceeds 15 or 20 per cent, we have only the "water spectrum." As the amount of water is still further decreased by the addition of more alcohol, the spectrum consists of the "water spectrum" and the "alcohol spectrum" superposed. As the amount of water is diminished below 15 per cent, the intensity of the water spectrum becomes less and less and the intensity of the alcohol spectrum greater and greater.

A question of importance in the present connection is this: Does the "water spectrum" gradually change over into the alcohol spectrum" as the amount of alcohol present is increased, or do we have here two separate and distinct spectra, the one corresponding to the aqueous solution, and the other to the alcoholic?

To test this point, we worked with fairly dilute solutions of neodymium chloride in water, in methyl alcohol, and in mixtures of water

and methyl alcohol. The object in using dilute solutions was to be able to study the structure of the bands in the different solvents. In the more dilute solutions the several parts of any given band would come out clearly and could be measured. The result was to show that the "alcohol spectrum" was quite different from the "water spectrum." It had different components and they were arranged in a different way within the bands.

In mixed solvents, then, the two spectra coexisted, and we did not have the one passing over into the other as we changed the composition of the mixture of alcohol and water. The "water" spectrum and "methyl alcohol" spectrum had equal intensities when the mixture of the water and methyl alcohol contained from 6 to 8 per cent of water.

Neodymium nitrate shows change in the spectra analogous to those manifested by the chloride, when dissolved in mixtures of water and one of the non-aqueous solvents. The change with the nitrate is not so striking as with the chloride.

Praseodymium chloride in mixtures of water and methyl alcohol shows the same general features as were manifested by the chloride of neodymium. In the case of praseodymium chloride there is this additional feature: in the alcoholic solution an entirely new band appears, having no analogue in the aqueous solutions. This new band in the ultra-violet is by far the most intense in the entire spectrum of praseodymium chloride. On adding water to the alcoholic solution this band entirely disappears. In this case the alcohol spectrum is quite different from the water spectrum.

These results show beyond question that the solvent plays an important role in the absorption of light by solutions. The question arises, what is this role? It is difficult, not to say impossible, to explain the action of the solvent on any other ground than that a part of the solvent combines with the ions and molecules of the dissolved substance, and the solvated parts have different resonance from the unsolvated. This means that they would absorb different wave-lengths of light. The alcoholates would have different resonance from the hydrates, whence the different absorption spectrum in alcohol from that in water.

We regard this evidence in favor of solvation in solution as important, and, as we shall see, many examples of "solvent" bands were brought to light in the investigation which followed.

WORK OF JONES AND STRONG.

The work of Jones and Anderson was continued by Jones and Strong.[1] They investigated a number of problems, including the effect of the solvent on the absorption of light by the dissolved substance. Jones and Anderson, as we have just seen, had found one good example

[1]Carnegie Inst. Wash. Pubs. Nos. 130 and 160. Amer. Chim. Journ., **43**, 37, 224 (1910); **45**, 1 (1910); **47**, 27 (1912). Phys. Zeit. **10**, 499 (1909). Phil. Mag., April, 1910. Journ. Chim. Phys., 8, 131 (1910).

of the existence of "solvent bands" in the absorption spectra of neodymium and praseodymium salts in water and the alcohols. The question arose, was this a phenomenon peculiar to these salts, or does the solvent play a general role in the absorption of light by solutions?

Jones and Strong attempted to answer this question by studying a large number of salts in a large number of solvents. They worked especially with salts of neodymium and uranium, because these substances had sharp absorption lines and bands whose positions could easily be determined with reasonable accuracy. Work was done not only with uranyl salts, but with uranous. A convenient method was found for reducing uranyl salts to the uranous condition, and uranous salts were found to have very sharp absorption lines.

Uranyl chloride was studied in the following solvents: water, methyl, ethyl, propyl, isopropyl, butyl, and isobutyl alcohols, glycerol, ether, methyl ester, and formamide. A comparison of the wave-lengths of the absorption lines and bands in these different solvents brought out the fact that the wave-lengths of some of the lines and bands differed considerably in the different solvents. The results here showed that the solvent unquestionably has much to do with the absorbing power of the solution, "solvent bands" appearing very frequently. The wave-lengths of a few of the different lines and bands of uranyl chloride in the above-named solvents have been tabulated,[1] and the table is here reproduced. It shows at a glance the different wave-lengths of the several lines and bands compared.

TABLE 51.—*Wave-lengths of uranyl chloride absorption lines.*

In water.....	λλ 4025,	4170,	4315,	4460,	4560,	4740, and 4920
In methyl alcohol....	λλ 4090,	4220,	4345,	4465,	4590,	4760, and 4930
In ethyl alcohol.....	λλ 4100,	4250,	....	4400,	4580,	4750, and 4900
In propyl alcohol.....	λλ 4100,	4230,	....	4400,	4580,	4750, and 4910
In isopropyl alcohol...	λλ 4100,	4250,	....	4360,	4560,	4750
In butyl alcohol.....	λλ 4100,	4240,	....	4390,	4560,	4750, and 4970
In isobutyl alcohol....	.....	....	....	λλ 4400,	4560,	4720, and 4900
In ether.....	λλ 4040,	4160,	....	4300,	4444,	.... and 4630
In methyl ester.....	λλ 4030,	4160,	4280,	4440,	4620,	4790, and 4920
In glycerol.....	λλ 4025,	4140,	4260,	4400,	4540,	4720, and 5050
In formamide.....	.....	....	....	λλ 4450,	4650,	.... and 4840

The absorption spectra of uranyl nitrate in mixtures of water and methyl alcohol were studied. The absorption in water was much less than in pure methyl alcohol. The addition of water to the alcoholic solution diminished the absorption. In the mixtures of water and methyl alcohol the absorption bands became very broad. A study of these broadened bands showed that they were the "alcohol" and "water" bands coexisting, and that one set of bands was not simply the other set shifted in position. The importance of this fact has already been referred to in the work of Jones and Anderson. It shows that the "alcohol" bands are fundamentally different from the "water"

[1]Journ. Franklin Inst., Dec. 1913, p. 528; also Phil. Mag., May 1912, p. 730.

bands. Further, the intensity of the solvent bands is a function of the relative amounts of the solvents that are present in the mixture. This, as has been pointed out, indicates the existence of hydrates in the aqueous solutions and of alcoholates in solutions in alcohol, these solvates having definite resonance and, therefore, definite absorption spectra.

One of the most striking examples of solvent bands is shown by the absorption spectra of uranous chloride and bromide in a mixture of water and methyl alcohol. We find two entirely distinct spectra, one belonging to each solvent. Some lines and bands appear in the one solvent which are entirely absent from the other, and practically all the lines and bands have very different positions in the two solvents. To see how differently the spectra appear, reference must be made to plate 23 of Publication No. 160 of the Carnegie Institution of Washington.

The spectrum of uranous chloride in water is not only different from the spectrum in methyl alcohol, but these are both different from the spectrum in acetone. If we compare the spectra of this salt in the three solvents, we might easily conclude that we were dealing with three fundamentally different spectra, and the only change is in the nature of the solvent.

Uranous salts in solvents other than the above also show very characteristic "solvent" bands. When ethyl alcohol is added to an aqueous solution of uranous chloride, a marked change is produced in the spectrum. The "ethyl alcohol" bands are quite different from the "water" bands. The alcohol bands, or the water bands, can be made the more intense by simply varying the relative proportions of the two solvents. The addition of acetone to an aqueous or methyl alcohol solution of uranous chloride produces a marked change in the spectra. A number of acetone bands appear, these being different from the "water" bands on the one hand, and from the "alcohol" bands on the other.

Uranous chloride dissolved in methyl alcohol has an absorption spectrum very similar to that in ethyl alcohol. This would be expected, on account of the close similarity of methyl alcohol and ethyl alcohol. The methyl alcohol bands are of slightly shorter wave-lengths.

The absorption spectra of uranous chloride in glycerol, and in mixtures of glycerol and water were also studied. A number of "glycerol" bands manifested themselves, the glycerol absorption being very different from that of water.

The absorption spectrum of uranous chloride in methyl alcohol and ether was also studied. The solution in methyl alcohol showed complete absorption in the ultra-violet to wave-length λ 3700, while the addition of ether extended the absorption to λ 3800. The addition of the ether caused the absorption to shift towards the red, the magnitude of this shift being from 10 to 30 Å. U.

It has already been pointed out that salts of neodymium are especially well adapted to the study of "solvent" bands, on account of the sharpness of the neodymium lines and bands, and the accuracy with which they can be measured. Neodymium salts were studied in a number of solvents, and a few of the results obtained are given below.[1]

ABSORPTION SPECTRA OF NEODYMIUM SALTS.

The following nomenclature will be used in describing the neodymium absorption spectra:

α group in the region λ3400 to λ3600.
β " at about λ4300.
γ " from λ4600 to λ4800.
δ " from λ5000 to λ5400.
ϵ " in the region λ5800.

In designating the neodymium spectra we start from the violet end of the spectrum. This is the natural method when a grating is used. It is doubtful whether, in the near future, the ultra-violet spectrum of neodymium can be studied much farther than we have done, so that this is the natural end of the spectrum at which to begin. It is, on the other hand, probable that there are many neodymium bands farther down in the infra-red than we have gone; and when these have been worked out they can then be named in the natural order.

The change in the absorption spectrum of neodymium chloride as the solvent is changed can best be seen by expressing the results in the following form: The abbreviations used are "d." diffuse, "fa." faint, "fi." fine, "h." hazy, "i." intense, "n." narrow, "sh." sharp, "st." strong, "we." weak, "wi." wide.

The following results obtained with neodymium chloride show the effect of the solvent on the absorption spectra of solutions of this compound. The bands of the different solvents have different wavelengths and different relative intensities.

Having found that the solvent played an important part in determining the absorption of light by the dissolved substances, Jones and Strong used *isomeric organic solvents*, to see whether such closely related compounds would affect differently the power of substances dissolved in them to absorb light. They prepared solutions of neodymium chloride in propyl and isopropyl alcohols, and in butyl and isobutyl alcohols, and photographed the absorption spectra of this salt in these isomeric solvents. The results show different absorption lines and bands in the isomeric solvents.

If we compare carefully the spectra of neodymium chloride in butyl and isobutyl alcohols, we find that the bands are weak and diffuse in isobutyl alcohol, and have different relative intensities from what they have in the butyl alcohol. The bands in butyl alcohol are very

[1]See Phil. Mag. May 1912, p. 737, from which the few following pages are taken; also, Journ. Franklin Inst. Dec. 1913, p. 531.

TABLE 52.—*Absorption spectra of neodymium chloride in certain solvents.*

α GROUP.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ	λλ	λλ	λλ	λλ	λλ	λλ
3390 we.	3475 fa.	3545 sh.	3460	3450 sh. n.	3455 we.	3520 we.
3465 n. st.	3505	3460	3510	3460 we.	3485 st.	3475 st.
3505 n. st.	.....	3490	3535	3492 d.	3515 we.	3550 st.
3540 n. st.	3560 wi. i.	3510 we.	.....	3535 sh. n.	3545	.....
3560	.....	3525 st.	.....	3545	3579	.....
.....	.....	3540 st. n.	.....	3560 d.	.....	.....
.....	.....	3560 we.	.....	.....	.....	.....
.....	.....	3580 we.	.....	.....	.....	.....

β GROUP.

4271 sh.	4290	4270 we.	4265	4265	4300 we.	4288 sh.
4290 n. we.	4325	4285	.....	4285	.....	4270 fi.
.....	.....	4330 wi. we.	.....	4300	.....	4305 fi.
.....	.....	4450 wi. we.	.....	.....	.....	.....

γ GROUP.

4610 h.	4700	4600 we. d.	4600 d.	.....	4700	4620
4645 we.	4780	4700	4690	.....	4730	4710
4685	4825	4770	4730	.....	4780	4730
4755 sh.	.....	4830	.....	.....	4830	4760
4820 wi.	.....	.....	.....	.....	4880 we.	4790
.....	.....	.....	.....	.....	.....	4840

δ GROUP.

5090 n.	5125 h.	5130 wi. d.	5100 wi. d.	5085 n.	5150	5120 wi. h.
5125 wi. h.	5180 h. fa.	5180 wi. d.	5320 wi. d.	5095 n. we.	5260	5170 n.
5205 i. n.	5220 i. n.	5220	.....	5130	5215	5190 n.
5222 i. n.	5245 i.	5230	.....	5200	5230	5230
5255 n.	5290 n.	5250	.....	5215	5250	5240
5315 fa. h.	5315 fa.	5290	.....	5240	5300	5250
.....	.....	5330 we.	.....	5270	.....	5270 we.
.....	.....	.....	.....	5300	.....	.....

ε GROUP.

5725 n. st.	5725 h.	5740	5720 d.	5750	5740 we.	5740 h.
5745 st.	5765 n.	5780	5780	5780	5810 st.	5790
5765 st.	5800 st.	5810	5810	5820	5850 st.	5805
5795	5835 i.	5850	.....	5860	5890	5820
.....	5860 h.	.....	.....	5900	5920	5850
.....	5895 fa.	.....	.....	5930	5950 we.	.....
.....	5925 fa.	.....	.....	.....	5995 we.	.....
.....	.....	.....	.....	.....	6920 we.	.....

much finer and sharper than they are in isobutyl alcohol. Further, the bands of neodymium chloride in isobutyl alcohol have slightly greater wave-lengths than in butyl alcohol.

To eliminate the possibility of the effect of the solvent on absorption spectra being due to anything inherent in the nature of neodymium chloride, the nitrate of neodymium was studied in the same way as the chloride.

The absorption spectra of neodymium nitrate in water, in methyl alcohol, in ethyl alcohol, in mixtures of these alcohols and water, in propyl and isopropyl alcohols, in butyl and isobutyl alcohols, in acetone and in mixtures of acetone and water, in ethyl ester and in formamide, were carefully photographed and studied. Results are given below in the case of neodymium nitrate only for the α bands.

α Bands.

In water.—Practically the same as the bands of neodymium chloride, but the bands of the nitrate are broader and hazier than those of the chloride.

In methyl and ethyl alcohols.—There are only two bands in the α group, λ 3465 and λ 3545.

In propyl alcohol.—$\lambda\lambda$ 3455, 3500, and 3585.

In isopropyl alcohol.—$\lambda\lambda$ 3460, 3505, and 3535.

In butyl alcohol.—$\lambda\lambda$ 3450, 3500, and 3540.

In isobutyl alcohol.—Ultraviolet absorption was so great that on the plate taken the α group did not appear. The absorption in general is the same as that of the chloride in this alcohol.

In acetone.—$\lambda\lambda$ 3475, and 3555.

In ethyl ester.—$\lambda\lambda$ 3455, 3500, and 3540.

The other groups of absorption bands of neodymium nitrate in the different solvents show differences in the wave-lengths comparable with the above; but these results suffice to show the effect of the solvent on the power of neodymium nitrate to absorb light.

The above is strong evidence that the solvent plays an important part in the absorption of light by substances dissolved in it. When we take into account the number of salts studied and the number of solvents employed, the evidence is little short of proof. The only reasonable question is, How are we to interpret these facts? Before attempting to answer this question we should take into account also the following fact: A salt dissolved in a given solvent is characterized by a definite absorption spectrum. When a salt is dissolved in mixtures of varying proportions of two solvents, *only two definite absorption spectra appear*, one being characteristic of each solvent. One spectrum *does not gradually change* into the other as the composition of the mixed solvent changes, but only the *relative intensities* of the two spectra vary. Starting with that mixture of the two solvents in which both of the spectra are equally intense, if we diminish the amount of *a* relative to *b*, the spectrum corresponding to *a* becomes feebler and feebler, and the spectrum corresponding to *b* more and more intense.

This fact was first noted by Jones and Anderson, and since repeatedly confirmed by the work of Jones and Strong. We found that when neodymium chloride was dissolved in a mixture of methyl alcohol and water, it showed a definite set of "water" bands and a definite set of "methyl alcohol" bands. As the amount of water in the solution was decreased relative to the alcohol, the "water" bands decreased in intensity but remained in the same position. As the amount of alcohol in the solution was decreased relative to the water, the "alcohol" bands decreased in intensity, but their position remained unchanged.

Jones and Anderson interpreted these facts as strong evidence in favor of the view that there are definite hydrates and definite alcoholates in the solution.

The spectroscopic evidence for solvation in solution furnished by Jones and Anderson has, as has already been stated, been increased many fold by the work of Jones and Strong. A large number of solvents and a fairly large number of salts have been used, and the existence of solvent bands in general has been established.

The question of the relative stability of the different solvates with respect to various physical and chemical agents has been studied at length by Jones and Strong by means of absorption lines and bands. It would lead us beyond the scope of this paper to discuss these results in detail. Suffice it to say that the hydrates in general are the most persistent of all the solvates, although this depends upon the conditions to which the solution is subjected.

Taking all of the spectroscopic work into account, I regard the evidence from this source as strongly supporting the solvate theory of solution as advanced by myself about fifteen years ago.

EFFECT OF RISE IN TEMPERATURE.

Jones and Strong studied the effect of rise in temperature on the absorption spectra of solutions. Considerable work had already been done on the effect of temperature on absorption spectra over the temperature range 0° to 100°. This temperature limit could be studied in open vessels. To work at higher temperatures closed apparatus must, of course, be used. Such apparatus was devised and used up to 200°.[1]

The general effect of rise in temperature is to increase the color of the solution of the inorganic salt, the solution becoming less transparent. The deepening of the color is usually due to a widening of the absorption bands. The widening of the bands with rise in temperature is frequently unsymmetrical.

While the effect of rise in temperature is to cause the long wave-length bands to increase in intensity, and in some cases to produce new bands, in some solvents the effect of rise in temperature is to cause the short wave-length bands to increase in intensity and even

[1]Carnegie Inst. Wash. Pub. No. 130.

to disappear. If the absorption is sufficiently intense so that each group of bands appears as a single band, these broad bands may widen very unsymmetrically towards the red as the temperature is raised.

In pure solvents the bands not only widen with rise in temperature, but the edges become more diffuse. With mixtures of salts such as calcium and neodymium chlorides, the bands become weaker with rise in temperature.

It is interesting to note that the absorption of a salt in mixtures of two solvents often decreases in intensity with rise in temperature. The effect of rise in temperature on the different "solvent bands" is often quite different. Uranous bromide in 40 per cent water and 60 per cent alcohol showed, at ordinary temperatures, the "water" and "alcohol" bands of equal intensity. When the temperature was raised to 80° the "water" bands practically disappeared, while the "alcohol" bands were scarcely widened at all.

While the effect of rise in temperature is to produce a change in the intensity of the "solvate" bands, it produces very little change in the wave-lengths of the bands. In some cases, in mixtures of water and alcohol, the alcohol bands increase in persistency as the temperature is raised. This is important as showing that the hydrates and alcoholates have different degrees of stability with respect to temperature. The effect of rise in temperature is, in general, to increase the absorption in the short wave-lengths.

An interesting question arose in connection with the effect of temperature on the solvates. Does rise in temperature produce a permanent change in the composition of the solvates? It would seem highly probable that it would not. The composition of any given solvate is determined by the amount of solvent relative to dissolved substance. If the complex solvate is rendered simpler by rise in temperature, then, when the solution cools down the solvate should have its original complexity—the original condition of equilibrium should be restored.

The results from absorption spectra confirm the above conclusion. When a salt is dissolved in a mixture of two solvents and the solution heated, there is, as we have seen, a change in the spectra. When the solution is cooled again the original spectrum is obtained. This shows that the original solvates are, as we would expect, reformed. This would seem to have some bearing on the nature of the solvates existing in solution. The idea that was originally advanced as to the composition of the hydrates existing in aqueous solution was that a large number of hydrates existed simultaneously in a given solution, the composition for any given substance and any given solvent being determined chiefly by the concentration of the solution, temperature being constant. In a word, we had simply a condition of equilibrium for any given substance between the combined and the free water. This condition of equilibrium would be changed with rise in temperature, some of the combined water being set free, in accordance with

the general principle that rise in temperature breaks down aggregates formed with evolution of heat, and most aggregates are formed with heat evolution.

If the original temperature is restored, the original conditions of equilibrium are reestablished and the initial solvates reformed. If there were only a few definite hydrates in any given aqueous solution, each of these would probably be stable over a definite range in temperature, and the changes in their composition would probably take place by jumps. This would produce correspondingly irregular changes in the absorption spectra, and not the regular transitions which were noted.

SPECTROPHOTOGRAPHY OF CHEMICAL REACTIONS.

The effect of adding an acid to uranium salts of another acid was studied at some length. Thus, uranyl nitrate was treated with sulphuric, hydrochloric, and acetic acids; uranous and uranyl acetates with various acids; a number of uranous salts and neodymium acetate with nitric acid, and so on. The salts and acids were selected so as to show the greatest spectroscopic changes. The action of nitric acid on uranous salts is especially interesting.

The spectrophotographs of chemical reactions show that, as the salt of one acid is transformed into the salt of another acid, the changes produced in the spectra are gradual. For example, when uranyl nitrate is transformed into uranyl sulphate, the uranyl nitrate bands gradually shift into the sulphate position. The details and data bearing on this point are given in Publication No. 130 of the Carnegie Institution of Washington. The addition of a large amount of sulphuric acid to a small amount of a solution of uranyl nitrate in nitric acid, showed admirably the gradual shift of the bands from the nitrate to the sulphate position.

The addition of a small amount of nitric acid to uranous acetate, does not appreciably oxidize the uranous salt. The uranous bands are shifted towards the violet.

The gradual shift of the absorption bands as one salt of a metal is transformed into another salt by the addition of more and more free acid is very important.

The work done in my laboratory, which, up to the time we are now discussing had had to do with about 5,000 solutions, had shown that any given series of absorption bands corresponds to a definite chemical condition of the dissolved substance. When a salt is treated with acid, the absorption bands of some of the salts shift gradually over to the position occupied by the bands corresponding to the new salt of the metal with the acid in question. In such a case the absorption bands can be made to occupy any position between the initial and final positions. It therefore seems probable that, when a salt of one acid is transformed in this way into a salt of another acid, a series of

intermediate systems or compounds is formed. These systems are for the most part too unstable to be isolated, at least by the methods now at our disposal; but the action of solutions on light makes their existence highly probable.

Our chemical equations of to-day represent, in general, only the beginning and end of chemical relations. They tell us little or nothing about the intermediate stages of chemical reactions, and these are the most interesting phases of the reaction. From our spectroscopic work we are forced to conclude that at least some chemical reactions are far more complex than would be indicated by the equations that we ordinarily use to express them. When, for example, a nitrate is transformed into a sulphate, there seems to be formed a series of intermediate systems, sulphonitrates or nitrosulphates. We know nothing about these substances chemically, but their existence is made highly probable by a purely physical method—the action of these substances on light.

This raises the question, are chemical reactions in general more complex than we ordinarily represent them to be? Do these intermediate systems exist in chemical reactions in general? It is impossible to study all reactions by the spectroscopic method, if, for no other reason, because many solutions do not have sharp and well-defined absorption. The reactions, however, which can be studied directly by the spectroscopic method do not seem to differ in any fundamental manner from those reactions which can not be so studied. They conform to the same laws that are obeyed by other reactions and are in every respect analogous to them. This leads to the conjecture that in those reactions which can not be studied spectroscopically, there are also intermediate systems or compounds which are too unstable to isolate; and since they do not have characteristic spectra, their presence can not even be detected. The formation of these intermediate systems is strictly in accord with the action of mass in chemistry. Some such intermediate compounds have in a number of reactions recently been isolated by methods now at our disposal. As methods become more refined, and we acquire better control of conditions, it seems not improbable that many more intermediate compounds will be isolated.

At present we can not isolate any large percentage of these intermediate systems on account of their instability. The best we can do is to study their properties in solution in the different solvents by purely physical methods. It is obvious that these intermediate systems must be studied if we are ever to know the real mechanism of chemical reactions, and not simply the conditions at the beginning and end of reactions. Other suggestions which have been offered to explain the gradual shift of the absorption bands as one salt is transformed into another, appear to be entirely inadequate, if not meaningless.

WORK OF JONES AND GUY ON THE ABSORPTION SPECTRA OF SOLUTIONS.

The work on the absorption spectra of solutions had, at the time that Guy began his investigation, been extended to between 6,000 and 7,000 solutions. In all of this work the grating spectroscope had been used, and the results recorded on a photographic plate. The photographic method recorded the positions of the various absorption lines and bands, but gave only a qualitative, or at best a roughly quantitative indication of the relative intensities of the various lines and bands. The photographic method is, generally speaking, a qualitative method.

If we are ever to discover relations of fundamental significance between the power of dissolved substances to absorb light and the nature of solution, we must have some quantitative method of studying the intensities of the absorption lines and bands and of the various parts of the same bands. With this idea in mind a very sensitive radiomicrometer was built and used to measure the intensity of absorption.

Before taking up this problem, Jones and Guy investigated two others by the photographic method. They studied the effect of temperature on the absorption spectra of aqueous solutions up to 200°. This required a specially designed apparatus which would not be attacked by the superheated water-vapor. It was found that while some of the bands of aqueous solutions are practically unaffected by rise in temperature, many of them widen as the temperature is raised. The widening of the absorption bands is usually not symmetrical, but is generally towards the red. The red edge widens out, becoming more hazy and diffuse, while the violet edge remains pretty sharp. The effect of rise in temperature on the absorption spectra of aqueous solutions is, then, often analogous to the effect produced by increasing the concentration of the solution. This is especially the case with solutions of praseodymium nitrate. The effect of dilution on absorption spectra was studied pretty thoroughly by Jones and Guy. It was well known that both molecules and ions can absorb light, and the question was, do they have the same or different absorption? Jones and Anderson[1] had shown that if they absorb differently, the difference is slight. To detect any such differences wide ranges in dilution must be employed.

Cells were devised for holding the solutions, which were 0.5 cm., 50 cm., and 250 cm. in length. The concentrations were varied in the same proportions as the lengths of the cells. If we call the concentration used in the shortest cell unity, 100 times as dilute a solution was used in the cell which was 50 cm. long, and this was diluted 5 times for the longest cell. It was found that many of the absorption bands of neodymium chloride and bromide widen as the concentration of the solution is increased. Some of the bands of neodymium sulphate and acetate show similar changes with increase in the concentration of the solution. The most marked changes, however, are produced with the bands of neodymium nitrate. Many of them show very pronounced

[1]Carnegie Inst. Wash. Pub. No. 110.

widening with increase in concentration. Solutions of praseodymium salts also show a widening of the absorption bands as the concentrations are increased, but these changes are less pronounced than with salts of neodymium. The absorption spectra of uranyl salts change more with change in concentration than the spectra even of salts of neodymium. The changes are in the same direction, the bands increasing in breadth with increase in concentration.

These results are what would be expected from the solvate theory of solution. As the concentration of the solution is changed, the complexity of the solvate about the molecules or ions is changed. It would seem that this ought to affect the resonance of the solvated resonator. As the concentration of the solution is increased the solvate becomes simpler and simpler. The vibrating particle surrounded by a simple solvate should show different absorption than when surrounded by a complex solvate. The above results show that such is the case, the more concentrated the solution the wider in general the absorption bands.

The radiomicrometer not only provides us with a method of studying absorption spectra quantitatively, but greatly extends the range of wave-lengths that can be studied. The earlier work with the very sensitive radiomicrometer had to do with the study of solutions of neodymium salts. The effect of dilution on absorption spectra was also investigated quantitatively by means of the radiomicrometer. It was found by this method, as with the grating and photographic plate, that the more concentrated the solution the broader the absorption bands. It was also found that in the more dilute solution, while the absorption bands were narrower, they were more intense. Further, in the more dilute solutions the centers of the bands were displaced towards the longer wave-lengths.

The most interesting and important result brought out by the work of Jones and Guy was the effect of the dissolved substance on the absorption of light by water. We noted that aqueous solutions of certain hydrated salts are more transparent than pure water. This is obviously a fact which called for careful study. We compared the absorption of aqueous solutions of strongly hydrated salts,with the absorption of a layer of water equal in depth to the water in the solution. Similar experiments were carried out with salts which are only slightly hydrated. The slightly hydrated salts with which we worked were potassium chloride and ammonium chloride and nitrate. It was necessary to select colorless salts which themselves had little or no absorption in the infra-red where water absorbs. It was found, in the earlier work, that the above-named compounds had nearly the same absorption as water having the same depth as the water in the solution; but in subsequent work this conclusion must be modified for certain substances near the bottoms of the absorption bands.

In terms of the solvate theory of solution, we should expect the absorption of the solution of a slightly hydrated salt in general not to

differ very greatly from that of so much pure water, since, when the solvent is not combined with the dissolved substance, it is difficult to see how either could affect appreciably the absorbing power of the other.

When we turned to the strongly hydrated salts, very different results were obtained. As examples of this class of substances we studied calcium and magnesium chlorides and aluminium sulphate. Take the results for a 5.3 normal solution of calcium chloride. The solution is more transparent from 0.9 μ to 1 μ. It is again the more transparent from 1.05 μ to 1.2 μ, being as much as 25 per cent more transparent than the solution. For the longer wave-lengths the water is in general the more transparent until 1.42 μ is reached, when both water and solution become equally opaque. Similar results were obtained with magnesium chloride.

Aluminium sulphate presents this peculiarity, that at 1 μ the solution is more transparent than the water. The obvious explanation of these surprising results seems to be that they must be due to some action of the dissolved substance on the solvent. Jones and Anderson[1] showed that the solvent can have a marked effect on the absorbing power of the solution in that solvent, even when the solvent itself had no absorption in the region in question.

A large number of examples of "solvent bands" were discovered by Jones and Strong.[2] They found many non-absorbing solvents which affected the absorption of the dissolved substance, and could even distinguish between certain organic solvents and their "iso" compounds by the "solvent bands" which manifested themselves. This action seems to have been satisfactorily explained as due to a combination of the solvent with the dissolved substance forming solvates. The solvate theory enables us to account for many facts which apparently could not be satisfactorily explained by the theory of electrolytic dissociation alone, as we have seen. The same theory seems to aid us in explaining the facts just described. Those compounds which do not form hydrates, or which form only very simple hydrates, such as potassium chloride and the like, show results such as would be expected. Their solutions are not more transparent than so much pure water. In general, the absorption of such solutions is of the same order of magnitude as that of the water in which they are dissolved. We shall see that it came out in later work that solutions of only slightly hydrated salts are more opaque than pure water at the centers of the absorption bands. This, however, does not affect at all the conclusions drawn above. It is only the hydrated salts whose solutions are appreciably more transparent than so much pure water. How does the solvate theory explain these facts?

The combined water seems to have less power to absorb light than free water. This would account for the above facts. The presence

[1]Carnegie Inst. Wash. Pub. No. 110. [2]*Ibid.*, Nos. 130 and 160.

of the salt seems to shift the absorption of the water towards the larger wave-lengths. Rise in temperature and increase in concentration shift the absorption of the salt towards the longer wave-lengths. The effect of rise in temperature and increase in concentration is to simplify the hydrates existing in the solution. Simplifying the resonator, then, shifts the absorption towards the red.

The effect of the salt on the absorption of the water, is the same as rise in temperature and increase in the concentration of the solution on the absorption of the dissolved substance. It may well be that the dissolved substance diminishes the association of the solvent and this simplifies the solvent resonator. This may be true, especially with water of hydration, which is more directly under the influence of the dissolved substance than the free water.

WORK OF JONES, SHAEFFER, AND PAULUS.

The result obtained by Jones and Guy was regarded as of such importance in its bearing on the solvate theory of solution, that it was thought desirable to repeat and elaborate with improved method the work which led to it. Certain details of method and manipulation were carefully studied, and the degree of accuracy of the procedure adopted was carefully ascertained. This has all been discussed in detail in the first chapter of this monograph. The non-hydrating or slightly hydrating salts, potassium chloride, ammonium bromide, and sodium nitrate, were studied. The strongly hydrated calcium chloride, magnesium chloride, magnesium bromide, magnesium sulphate, magnesium nitrate, zinc sulphate, and zinc nitrate were investigated at varying concentrations and depths of layers.

Solutions of the strongly hydrated salts have in general greater transparency than pure water, especially at the centers of the absorption bands. As the regions of intense absorption are approached in the longer wave-lengths, the solution is much more transparent than the pure solvent. This difference may amount to as much as 40 per cent.

The non-hydrated or only slightly hydrated salts give results which, in many respects, are exactly the opposite of those obtained with hydrated salts. In the three cases studied, the solution had greater absorption than the solvent at the centers of the bands. This is precisely the opposite of what was found for the strongly hydrated salts. Regions of the spectrum, for which solutions of hydrated salts were as much as 40 per cent more transparent than the solvent, show for non-hydrated salts that the solution is 40 per cent less transparent.

It was pointed out that the results obtained could be best explained by the solvate theory of solution. Indeed, this evidence is of the very strongest for that theory. In the solutions studied, more than half of the water was shown to be combined with the dissolved substance. It was shown that this would certainly alter the vibrational frequency or resonance of the absorbing systems.

The transmission curves obtained seem to justify the conclusion that combined water has less power to absorb light than uncombined. We have been able to find no other rational explanation which would account satisfactorily for our results. The difference in the behavior of hydrated and non-hydrated salts seems unquestionable.

Any attempt to explain such a difference as the above on the ground of a change in the dielectric constant of the medium does not appear to have a good physical basis. Why the presence of the one class of salts alters the dielectric constant of the medium differently from the other class, is a question that would have to be answered. This attempt to explain our results does not appear to be much more than words. We regard, then, the spectroscopic evidence in its bearing on the solvate theory of solution as among the most important. The presence of definite "solvent bands" in the different solvents and the difference between the absorption of aqueous solutions of non-hydrated and strongly hydrated salts are to be counted as among the strongest and most direct lines of evidence thus far brought to light in my laboratory bearing on the solvate theory of solution.

SUMMARY OF THE LINES OF EVIDENCE OBTAINED IN THIS LABORATORY BEARING ON THE SOLVATE THEORY OF SOLUTION.

The following lines of evidence bearing on the solvate theory of solution have, then, been established in this laboratory.[1]

1. Relation between lowering of the freezing-point of water and water of crystallization of the dissolved substance.
2. Approximate composition of the hydrates formed by various substances in solution.
3. Relation between the minima in the freezing-point curves and the minima in the boiling-point curves.
4. Relation between water of crystallization and temperature of crystallization.
5. Hydrate theory in aqueous solutions becomes the solvate theory in solutions in general.
6. Temperature coefficients of conductivity and hydration.
7. Relation between hydration of the ions and their ionic volumes.
8. Hydration of the ions and the velocities with which they move.
9. Dissociation as measured by the freezing-point method and by the conductivity method.
10. Effect of one salt with hydrating power on the hydrates formed by a second salt in the same solution.
11. Investigations in mixed solvents.
12. Spectroscopic evidence bearing on the solvate theory of solution; work of Jones and Uhler.
13. Work of Jones and Anderson on absorption spectra, in which the presence of "solvate" bands was first detected. This showed that

[1]See Journ. Franklin Inst., Dec. 1913.

the solvate had an effect on the absorption of light, and this could be explained only as due to a combination between the solvent and the resonator, or something containing the resonator.

14. The work of Jones and Strong on absorption spectra established the existence of a larger number of "solvent" bands. They showed that these were formed by many salts and in many solvents. They could even distinguish between the bands of a salt in a given alcohol and in its isomer. This was regarded as very important. The temperature work of Jones and Strong was strong evidence for the solvate theory.

15. The work of Jones and Guy on the effect of high temperature on the absorption spectra of aqueous solutions, and also on the effect of dilution, led to results which were all in keeping with the solvate theory.

The most important spectroscopic work of Jones and Guy, which bears on the solvate theory of solution, is that in which the radiomicrometer was used. It was here shown that solutions of certain strongly-hydrated non-absorbing salts are *more transparent* than pure water having a depth equal to that of the water in the solution. In the case of non-hydrated salts the solution was the more opaque. This shows that water in combination with the dissolved substance—water of hydration—has less absorption than pure, free water. This is regarded as striking evidence that some of the water in the presence of salts which are shown by other methods to hydrate is different from pure, free, uncombined water; and the simplest explanation seems to be that this is the combined water, or the water of hydration.

16. The work of Jones and Guy was repeated and extended by Jones, Shaeffer, and Paulus. They obtained results of the same general character as those found by Jones and Guy. Solutions of hydrated salts were in general more transparent than pure water, especially at the centers of the absorption bands. Solutions of non-hydrated or only slightly hydrated salts are more opaque than pure water, especially at the centers of the bands.

The above sixteen lines of evidence all point to the general correctness of the view that when a salt is dissolved in a solvent there is more or less combination between the salt, or the ions resulting from it, and the solvent. The magnitude of this solvation depends upon the nature of the substance and of the solvent.

HOW THE PRESENT SOLVATE THEORY OF SOLUTION DIFFERS FROM THE OLDER HYDRATE THEORY.

The present solvate theory of solution is not simply one of several possible suggestions which accounts for a certain class of experimental facts. It is the only suggestion that has thus far been made which seems to account satisfactorily for all of the facts established. Most of the above sixteen lines of evidence bearing on solvation in solution were obtained as the direct result of experimental work suggested by the solvate theory and carried out to test this theory. Many of the

results were predicted from this theory before a single experiment was carried out. Solvation, then, being accepted, as now seems pretty generally the case, the question arises, how does the present solvate theory of solution differ from the older hydrate theory of Mendeléeff, which has long since been abandoned as untenable?

Mendeléeff's theory was that certain hydroscopic substances, such as calcium chloride, sulphuric acid, and the like, formed a few definite hydrates when in the presence of water. Thus, sulphuric acid formed the hydrates $H_2SO_4.2H_2O$, $H_2SO_4.6H_2O$, $H_2SO_4.100H_2O$.

This view of Mendeléeff was proposed as the result especially of measuring the specific gravities of aqueous solutions of such compounds at different dilutions. When the specific gravities were plotted against the concentrations, the curve was not a continuous one, but showed a number of breaks. These breaks Mendeléeff could account for by assuming that certain definite hydrates or compounds between water and the dissolved substances existed at these concentrations. This was among the most important evidence brought to light bearing on the so-called hydrate theory of Mendeléeff.

This suggestion of Mendeléeff, based upon such inadequate evidence, should not be called a theory. It is scarcely worthy of the name hypothesis. Before a suggestion becomes a theory there should be a fair amount of evidence supporting it, and showing not only that the suggestion accounts for the facts, but that it is the only suggestion which will account for them. This was lacking in the so-called Mendeléeff hydrate theory.

The present solvate theory of solution may claim to have a fairly good experimental support, as the above review of the evidence obtained in this laboratory will show. In aqueous solutions hydration is a general phenomenon. Some substances combine with very little water, but most salts combine with very large amounts of water, the amount of combined water for any given substance being a function of the concentration of the solution and of the temperature. The more dilute the solution the larger the amount of the solvent combined with the dissolved substance—the more complex the hydrate. The lower the temperature the more complex the solvate. These solvates are very unstable; indeed, so unstable that it seems better to call them systems than definite chemical compounds. Anything so easily broken down by rise in temperature could hardly be called a chemical compound. Here, again, the present solvate theory differs from the older hydrate theory.

While there is some spectroscopic evidence pointing to the existence in solution of a certain definite hydrate, or certain definite hydrates, we have obtained a large amount of evidence which seems to indicate the existence in aqueous solutions of a large number of hydrates, or indeed of a whole series of hydrates, the composition depending primarily on the concentration of the solution. While this is not essential

to the present solvate theory of solution, it would differentiate it fundamentally from the older hydrate theory.

The present theory is not simply a hydrate theory of aqueous solutions. Evidence has been obtained, and is herein briefly discussed, which shows that solvents other than water combine with the dissolved substance. This has been established for the alcohols by the boiling-point method, and for the alcohols and many other solvents by spectroscopic investigations. Indeed, enough evidence has already been obtained to make it highly probable that solvation is not limited to aqueous solutions, but is a general property of solutions. Solvents in general have more or less power to combine with substances dissolved in them—in a word, *we have the solvate instead of simply a hydrate theory.*

A method has been worked out in this laboratory for determining the approximate composition of the hydrates existing in aqueous solutions. This makes the present theory useful scientifically. We can now determine approximately the amount of "combined" and the amount of "free" water existing in any given aqueous solution. Thus, our theory is placed upon a workable basis, and enables us to determine, in any given case, how much of the liquid present is really playing the role of solvent.

The evidence pointing to the general correctness of the solvate theory of solution is, then, so strong that it seems that this conception is in accord with a fundamental condition in connection with the nature of solution.

Further, our solvate theory of solution is very different from the earlier, unproved hydrate theory of Mendeléeff.

The question now arises, of what scientific significance or value is the establishing of the fact that there is more or less combination between the dissolved substance and the solvent?

SIGNIFICANCE OF THE SOLVATE THEORY OF SOLUTION.[1]

The evidence for the solvate theory of solution, which has been furnished in this laboratory as the result of somewhat more than a dozen years of investigation, has recently been brought together and briefly discussed.[2] The evidence is so unambiguous and convincing, that ions and some molecules combine with more or less of the solvent, that it seems that it can now be accepted as a fact of science.

This, however, raises a number of questions: What relation does the solvate theory of solution bear to the theory of electrolytic dissociation?

Does the solvate theory help us to explain any of the apparent discrepancies in the theory of electrolytic dissociation? Does the solvate theory help us to explain the facts of chemistry in general and of physical chemistry in particular? Why is the nature of solution so important, not only for chemistry but for science in general?

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[1]This section is taken directly from my paper in the Journal of the Franklin Institute, Dec. 1913.
[2]Zeit. phys. Chem., **74**, 325 (1910).

THE SOLVATE THEORY AND THE THEORY OF ELECTROLYTIC DISSOCIATION.

When Arrhenius proposed the theory of electrolytic dissociation, the question was not even raised as to the condition of the ions in the solution, except that they behave as if they existed independently of one another in solution. The theory simply said that molecules of acids, bases, and salts, in the presence of a dissociating solvent like water, break down to a greater or less extent into charged parts called ions, the cations or positively charged parts being electrically equivalent to the anions or negatively charged parts. The cations are usually simple metallic atoms carrying one or more unit charges of positive electricity. The cation might, however, be more or less complex, as illustrated by ammonium and its substitution products. The anion is usually complex, consisting of a larger or smaller number of atoms. It may, however, be an atom carrying negative electricity, as in the case of the halogen acids and their salts.

The degree of dissociation is determined by the nature of the acid, base, or salt. Strong acids and bases are greatly dissociated. Indeed, the degree of dissociation determines their strength. Nearly all of the salts are strongly dissociated compounds, there being, however, some exceptions, as, notably, the halogen salts of mercury, cadmium, and zinc. There are, however, considerable differences in the amounts to which salts in general are dissociated at the same dilution.

The quantitative evidence furnished by Arrhenius and others for the theory of electrolytic dissociation is so convincing that few chemists of any prominence, who have carefully examined the evidence, have ever doubted the general validity of the theory; and the theory has become substantiated by such an abundance of subsequently discovered facts that it has now become a law of nature and a fundamental law of chemical science.

Arrhenius saw and pointed out clearly the importance of ions for chemistry; Ostwald and his pupils have shown that chemistry is essentially a science of the *ion*, molecules for the most part being incapable of reacting chemically with molecules; and Nernst has proved that the ion is the active agent in all forms of primary cells.

The theory of electrolytic dissociation, as already stated, does not raise the question as to the relation between the ion and the solvent. At the time that the theory was proposed, chemists did not know, and probably had no means of finding out, whether the ion is or is not combined with the solvent in contact with it. The solution of this problem remained for subsequent work.

Some of the many lines of evidence that ions and certain molecules are combined with a larger or smaller number of molecules of the solvent, and in many cases with a very large number of molecules of the solvent, have been recently discussed briefly by Jones in an article in

the *Zeitschrift für physikalische Chemie.*[1] The amount of the solvent combined with an ion is primarily a function of the nature of the ion or ions in the solution. It is, however, conditioned very largely by the dilution of the solution, and also by the temperature.

The evidence, some of which is given in the paper referred to above, and the remainder in other publications, of the results of investigations carried out in this laboratory during the past fifteen years, shows that the power of the ions to combine with the solvent is by no means limited to water and aqueous solutions, but is a property of solutions in general. The alcohols, acetone, glycerol,[2] etc., combine with certain substances dissolved in them; and it seems more than probable that all solvents combine with the dissolved substances to a greater or less extent. In a word, we do not have simply a theory of hydration, but a theory of solvation in general, which is an essential part of any generalization that would take into account the facts presented by solution.

The solvate theory of solution has been regarded in some quarters as a rival of the electrolytic dissociation theory of solution, if not directly antagonistic to it. Such is not at all the case. The solvate theory begins where the theory of electrolytic dissociation ends. The latter gives us the ions from molecules, and the former tells us the condition of the ions in the presence of a solvent after they are formed.

The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution.

DOES THE SOLVATE THEORY HELP TO EXPLAIN ANY OF THE APPARENT EXCEPTIONS TO THE THEORY OF ELECTROLYTIC DISSOCIATION?

Given the theory of solvation in solution together with that of electrolytic dissociation, the first question that arises is, does the former really aid us in explaining the phenomena presented by solutions?

Shortly after the theory of electrolytic dissociation was proposed, it was recognized and repeatedly pointed out, that after all it is only a theory of "ideal solutions," *i. e.*, very dilute solutions. It was shown not to be able to explain many of the phenomena presented by even fairly concentrated solutions. Indeed, it frequently could not deal quantitatively with the very solutions with which we work in the laboratory. The explanation of this shortcoming was not fully seen, and an analogy was resorted to. It was pointed out that the laws of Boyle and Gay-Lussac for gases hold only for "ideal gases," *i. e.*, dilute gases, but do not hold for gases of any considerable concentration.

It was stated that the gas laws when applied to solutions could not be expected to hold more generally than when applied to gases, and there the matter was allowed to rest.

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[1] "Evidence obtained in this laboratory during the past twelve years for the solvate theory of solution." Zeit. phys. Chem., **74**, 325 (1910).

[2] "Conductivity and viscosity in mixed solvents," by H. C. Jones and co-workers, Carnegie Inst. Wash. Pub. Nos. 80 and 180.

In the early days of the theory of electrolytic dissociation it was, however, pointed out that we have a fairly satisfactory explanation of why the simple gas laws do not hold for concentrated gases, this being expressed in the equation of Van der Waals; while no analogous explanation was offered in the case of solutions. That this point was well taken is obvious. A theory of solution, to be of the greatest value, must be applicable to all solutions, regardless of the nature of the substance, regardless of the nature of the solvent, and regardless of the concentration of the solution.

The explanation of these apparent exceptions to the theory of electrolytic dissociation presented by concentrated solutions has been furnished by the solvate theory. We now know that, for solutions in general, a part of the solvent is combined with the dissolved substance. While the amount of the solvent combined with any one ion is greater the more dilute the solution, at least up to a certain point, the total amount of the solvent in combination with the dissolved substance is greater the more concentrated the solution.

That the amount of combined solvent may become very great, even relative to the total amount of solvent present, can be seen from the following facts: In a normal solution of calcium chloride about two-fifths of the total water present is combined with the dissolved substance. In a three-normal solution of calcium chloride about five-sevenths of the total water is combined.

In the case of a normal solution of aluminium chloride in water, about five-eighths of the water present is combined with the dissolved substance, while in a two-normal solution about five-sixths of the water present is in a state of combination.

What we suppose to be a normal solution of calcium chloride is, therefore, more than $1\frac{1}{2}$ times normal, while what we suppose to be a three-normal solution is in reality more than eight times normal. In the case of aluminium chloride, what we suppose to be a normal solution is more than twice normal, while what we prepare as a twice normal solution is about twelve times normal.

These few facts, taken from thousands of a similar character, show that even fairly concentrated solutions are much more concentrated than we would suppose from the method of their preparation; while very concentrated solutions are many times more concentrated than, without the facts of solvation, we should be led to expect.

The general conclusion is that even fairly concentrated solutions are much stronger than if no solvation occurred, and are much more concentrated than we are accustomed to consider from the amount of substance added to a given volume of the solution—more or less of the water present being in combination and only the remainder playing the role of solvent. Without the theory of solvation, we have hitherto regarded all of the water present as acting as solvent.

We should, therefore, not expect the laws of gases to apply to such solutions, when we had no idea what was their concentration. Now that we know their concentration, we find that the laws of gases are of as general applicability to solutions as to gases, holding not simply for dilute, but also for concentrated solutions.

The theory of electrolytic dissociation, supplemented by the theory of solvation, is, then, not simply a theory of dilute or "ideal" solutions, but a theory of solutions in general.

DOES THE SOLVATE THEORY AID IN EXPLAINING THE FACTS OF CHEMISTRY IN GENERAL AND OF PHYSICAL CHEMISTRY IN PARTICULAR?

To answer this question at all fully would lead us far beyond the scope of this monograph. A few facts bearing upon this question can, however, be taken up. Take, for example, the action of the hydrogen ion both in the formation and saponification of esters. In the presence of the alcohols the hydrogen ion accelerates greatly the velocity with which an ester is formed, while in the presence of water it causes the ester to break down into the corresponding acid and alcohol.

In terms of ordinary chemical conceptions it is difficult, not to say impossible, to interpret these reactions, the hydrogen ion under one set of conditions undoing what under other conditions it effected.

In terms of the solvation theory these reactions admit of a very, simple interpretation. While the hydrogen ion is not strongly solvated, work in this laboratory has shown that all ions are more or less solvated. In the presence of alcohol the hydrogen ion therefore combines with a certain amount of this solvent. The hydrogen ion, plus the alcohol combined with it, unites with the organic acid, forming complex alcoholated ions which then break down yielding the ester.

On the other hand, the hydrogen ion in the presence of water combines with a certain amount of this solvent. The hydrated hydrogen ion, together with the water united with it, combines with the ester, forming a complex hydrated ion, which then breaks down into the corresponding acid and alcohol setting the hydrogen free again. For a fuller discussion of this reaction see the paper by E. Emmet Reid.[1]

A reaction analogous to the above is that of hydrogen ions on amides in the presence of water on the one hand, and alcohol on the other hand. In the presence of water the hydrated hydrogen ion combines with the amide, forming a complex hydrated ion which then breaks down yielding ammonia and acid, the ammonia, of course, combining with the acid.

In the presence of alcohol the alcoholated hydrogen ion combines with the amide, forming a complex alcoholated ion, which then breaks down into ammonia and the ester of the acid in question.

Hydrogen ions in a mixture of water and alcohol, which would contain both hydrated and alcoholated hydrogen ions, give both reactions

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[1] Amer. Chem. Journ., **41**, 504 (1909).

simultaneously; but, as Reid has pointed out, in the presence of an equal number of molecules of water and alcohol, the tendency of the hydrogen ion to hydrate is greater than the tendency to form alcoholates; and under these conditions the first reaction proceeds much more rapidly than the second.[1] A very large number of types of reactions could be discussed illustrating this same point, *i. e.*, the value of the solvate theory in interpreting chemical reactions.

When we turn to physical chemical processes, the solvation of the ions has to be taken into account at every turn. The velocities of the ions are, of course, a function of the degree of their solvation; and the behavior of the ions, both chemically and physically, is a function of their velocities. The effect of dilution, and especially of temperature on reaction velocities, is largely a question of the velocities of the ions present, which, in turn, are a function of the degree of their solvation.

In determining the actual concentration of a solution, the amount of the solvent combined with the ions must be taken into account, as has already been pointed out; and without knowing the actual concentrations of solutions quantitative chemistry would be impossible.

The solvate theory has thrown a flood of light on the whole subject of the conductivity of solutions, or the power of the ions to carry the electric current. It has shown us why the conductivity of lithium salts is less than that of sodium and potassium, notwithstanding the fact that the lithium ion is much smaller and lighter than the atom of sodium or potassium. We now know that the lithium ion is much more hydrated than the ions of these elements, and the mass of the moving ion is really much greater in the case of lithium.

When we come to the temperature coefficients of conductivity, the solvate theory has enabled us to interpret results which, without its aid, would be meaningless. We now know why ions with the greater hydrating power have the larger temperature coefficients of conductivity. We know why ions with the same hydrating power have approximately the same temperature coefficients of conductivity, and why dilute solutions have larger temperature coefficients of conductivity than concentrated solutions;[2] and, did space permit, we could multiply examples, almost without limit, of the effect of the solvate theory on physical or general chemistry.

WHY IS THE NATURE OF SOLUTIONS OF SUCH VITAL IMPORTANCE NOT ONLY FOR CHEMISTRY BUT FOR SCIENCE IN GENERAL?

The fact is well recognized that modern physical or general chemistry has reached out into nearly every branch of science, and has had an important influence on many of them. The question arises: Why is this the case? The answer is that physical or general chemistry is primarily a science of solutions.

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[1] Amer. Chem. Journ., **41**, 509 (1909). [2] *Ibid.*, **35**, 445 (1906).

This answer may not at first appear to be self-evident, but a moment's thought will show its general correctness. The whole science of chemistry is primarily a branch of the science of solutions in the broad sense of that term. By solutions is meant not simply solutions in liquids as the solvent, but solutions in gases and in solids as well; and not simple solutions at ordinary temperatures, but also at elevated temperatures. If we think of chemical reactions in general, we will realize what a small percentage of them takes place out of solution. Therefore, the nature of solutions is absolutely fundamental for chemistry. This applies not simply to general chemistry, including the chemistry of carbon, but also to physiological chemistry, which deals almost entirely with solutions in one solvent or another.

When we turn to physics we find solutions not playing as prominent a role as in chemistry, but nevertheless coming in in many places. The primary cells, secondary cells, electrolysis, polarization, diffusion, viscosity, surface-tension, are all phenomena in which the physicist is interested, and all depend for their existence upon solution.

When we turn to the biological sciences we find that solution is almost as important as for chemistry. Take animal physiology; here we have to deal very largely with solution in the broad sense of that term. The same remark applies to physiological botany; and solutions are very important for both animal and vegetable morphology, especially in their experimental developments. Bacteriology is fundamentally connected with solutions, and pharmacology is based upon solutions either without or within the body of the animal.

Solution in the broad sense is as fundamental for geology as for chemistry. The igneous rocks were solutions of one molten mass in another; and sedimentary deposits came down for the most part from solutions true or colloidal in water. The minerals crystallized out from solutions, and solutions of various substances, such as carbon dioxide, are to-day weathering the rocks and continually changing the appearance of the face of the globe.

An examination of facts such as those referred to above will show that the relation of physical or general chemistry to solutions is the prime reason why physical or general chemistry is so closely related to so many other branches of natural science. This alone would show the importance of a true and comprehensive theory of solutions, not alone for physical or general chemistry, but for the natural sciences in general.

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